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PB-287 140

Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals

Illinois State Geological Survey, Urbana

Prepared for

Municipal Environmental Research Lab, Cincinnati, OH

Aug 78

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA 600/2-78 157
August 1978

PB 287140

Research and Development

EPA

Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-78-157

2.

3. RECIPIENT'S ACCESSION NO.
PB287140

4. TITLE AND SUBTITLE
ATTENUATION OF POLLUTANTS IN MUNICIPAL LANDFILL LEACHATE BY CLAY MINERALS

5. REPORT DATE
August 1978 (Issuing Date)

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
R. A. Griffin and N. F. Shimp

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Illinois State Geological Survey
Urbana, Illinois 61801

10. PROGRAM ELEMENT NO.
1DC618

11. CONTRACT/~~GRANT~~ NO.
68-03-0211

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory--Cin., OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final Report 12/72 to 8/75

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer: Mike H. Roulier (513) 684-7871

16. ABSTRACT

The first part of this project was a laboratory column study of attenuation of pollutants in municipal solid waste landfill leachate by mixtures of sand and calcium-saturated clays. Chloride, Na, and COD were relatively unattenuated by passage through the clay columns; K, NH_4, Mg, Si, and Fe were moderately attenuated; and the heavy metals Pb, Cd, Hg, and Zn were strongly attenuated even in columns with small amounts of clay. Calcium, B, and Mn were higher in column effluents than in the applied leachate. Precipitation was the principal attenuation mechanism for the heavy metals; cation exchange was responsible for any attenuation of the other elements. The clays, in order of increasing attenuation capacity, were Kaolinite, Illite, Montmorillonite.

The second part of the project involved batch studies of adsorption of Cr, Cu, Pb, Cd, Hg, and Zn by Montmorillonite and Kaolinite from water solutions and from landfill leachate. Adsorption of the cations Cr(III), Cu, Pb, Cd, Hg, and Zn increased with increasing pH; adsorption of the anions Cr(VI), As, and Se decreased with increasing pH. Above pH ≃ 5.3 precipitation of the cations was an important mechanism while adsorption was the principal mechanism for the anions over the pH range studied. Because adsorption/mobility of any element was affected by other solutes in leachate, adsorption information on one leachate may not be directly applied to predicting adsorption of the same element at the same concentration in another leachate.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Attenuation *Transport Properties *Soil Chemistry Contaminants Arsenic Cadmium Copper	Industrial Wastes Chromium Iron Lead (Metal) Mercury (Metal) Selenium Zinc	Pollution Hazard Rating Chemical Oxygen Demand Groundwater Pollution Clay Liners Municipal Solid Waste Leachate Ammonium (ion)	13B

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 159
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE PCA08

EPA Form 2220-1 (Rev. 4-77)

U. S. GOVERNMENT PRINTING OFFICE: 1978-757-140/1445 Region No. 5-II

EPA-600/2-78-157
August 1978

ATTENUATION OF POLLUTANTS IN MUNICIPAL LANDFILL LEACHATE BY CLAY MINERALS

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CINCINNATI, OHIO 45268

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development, that necessary first step in solving a problem, involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; it is a most vital communications link between the researcher and the community.

This report presents results from laboratory investigation of the capacity of clay minerals to remove pollutants from municipal landfill leachates. These results are applicable to the design of clay mineral liners for sanitary landfills and to the land disposal of municipal and hazardous wastes.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

The first part of this project was a laboratory column study to evaluate the potential of mixtures of sand and calcium-saturated clay minerals for attenuating and preventing pollution of water resources by pollutants in municipal solid waste landfill leachate. Chloride, Na, and water-soluble organic compounds (COD) were relatively unattenuated by passage through the clay-sand columns; K, NH_4, Mg, Si, and Fe were moderately attenuated; and heavy metals -- such as Pb, Cd, Hg, and Zn -- were strongly attenuated by even small amounts of clay. Concentrations of Ca, B, and Mn in the column effluents increased markedly over the original leachate concentrations.

Montmorillonite was found to have the highest attenuation capability, followed by illite and then kaolinite. Precipitation, with resultant accumulation in the surface layers of the columns, was found to be the principal attenuation mechanism for the heavy metals Pb, Cd, Hg, and Zn. The cation exchange capacity of the clay minerals was concluded to be the dominant attenuation mechanism responsible for removal of other substances from the leachate.

The second part of the project involved batch studies of adsorption of Cr, Cu, Pb, Cd, Hg, and Zn by montmorillonite and kaolinite from water solutions and from landfill leachate. The adsorption in leachate proved to be 50 to 90% lower in most cases than the clays' adsorption capacity for the metal ions in pure aqueous solutions. The adsorption of the cations Cr(III), Cu, Pb, Cd, Hg, and Zn increased with increasing pH while the anions Cr(VI), As, and Se decreased with increasing pH. At pH values greater than about 5.3, precipitation of the heavy metal cations was found to be an important attenuation mechanism while adsorption was the principal mechanism for the anions over the entire pH range studied.

Pollutant adsorption by clay minerals (and hence the mobility of pollutants in clays and clay soils) was significantly affected by other, non-hazardous solutes in the leachates. This effect was so pronounced that information on movement of pollutants in one landfill leachate cannot be directly applied to predicting the movement of the same pollutants present at the same concentrations in a different landfill leachate.

To evaluate the relative pollution hazard for municipal leachates, a ranking system was developed. Results of the study are applicable to the use of clay minerals as liners for sanitary landfills and to the land disposal of municipal and hazardous wastes.

This report was submitted in fulfillment of Contract Number 68-03-0211, by the Illinois State Geological Survey, under the partial sponsorship of the Environmental Protection Agency. Work was completed as of August 1975.

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ACKNOWLEDGMENTS

In addition to the authors listed, the following were involved in writing parts of this report: A. K. Au, Keros Cartwright, R. R. Frost, R. H. Gilkeson, G. M. Hughes, G. D. Robinson, R. R. Ruch, J. D. Steele, and W. A. White. Their names are also listed in a footnote at the beginning of each section to which they contributed.

The authors gratefully acknowledge the U.S. Environmental Protection Agency for partial support of the work under Contract No. 68-03-0211, Cincinnati, Ohio; the American Colloid Company, Skokie, Illinois, for supplying the montmorillonite clay; the Minerva Company, Elizabethtown, Illinois, for supplying the illite clay; and the Ottawa Silica Company, Ottawa, Illinois, for supplying the quartz sand used in this study.

The authors also wish to give thanks to those Geological Survey staff members who gave freely of their time and talents. Among those are J. M. Mellske, D. R. Dickerson, R. H. Shiley, W. J. Armon, J. K. Kuhn, J. A. Schleicher, L. R. Camp, G. B. Dreher, J. K. Frost, L. R. Henderson, M. C. Charles, S. K. Friesen, R. M. Trandel, and D. B. Heck.

Special thanks go to R. J. Helfinstine and W. E. Cooper for special equipment and to P. L. Johnson for typing assistance.

SECTION 1

INTRODUCTION

During the past 30 years, the landfill method for disposal of municipal and industrial waste has been widely used in the United States. More than 90% of our nation's wastes are now placed on the land for ultimate disposal at the approximately 14,000 landfills throughout the nation (Garland and Mosher, 1975). These 14,000 landfills accept more than 360 million tons of household, commercial, industrial, and municipal solid waste per day, at a cost of more than 4.5 billion dollars annually (Black et al., 1968). As industry in the United States complies with the Clean Air Act and the Federal Water Pollution Control Act, the volume of industrial solid wastes, sludges, and liquid concentrates of pollutants is expected to double in the next 10 years. The disposal of such huge volumes of solid waste by landfilling is not without its environmental impact. When refuse buried in a landfill comes in contact with water, then leachate, a mineralized liquid high in organic substances, is produced and may move out of the fill and pollute the ground water.

Garland and Mosher (1975) have cited several examples of pollution by leachates migrating from landfills. An example of severe economic damage incurred by pollution of a drinking water aquifer by leachate from a landfill occurred in New Castle County, Delaware (Apgar and Satterthwaite, 1975). Leachate from the landfill migrated more than 800 feet and contaminated the Potomac drinking water aquifer 4 years after the landfill site had been closed. The drinking water was contaminated with such high levels of organic compounds and metal ions that it was no longer potable. To date, this problem has cost the county $800,000 for interim solutions and, if the dump must be moved to completely remedy the situation, the cost may reach as high as 20 million dollars. In addition to the monetary costs, the county estimates that it will take 10 years to restore full use of the aquifer.

In another case, reported by Garland and Mosher (1975), contamination of ground water by selenium was found to extend more than 2 miles from a dump site in Long Island. In this case as elsewhere, heavy-metal contamination may impart no odor or color to indicate that the water is contaminated.

The solid waste problem is most acute in the metropolitan areas, where competition for the available land is intense. A city of 2 million inhabitants generates 5000 tons of solid waste per day (Wirenius and Sloan, 1973), which rapidly fills the conveniently situated landfill locations. The problem of finding environmentally acceptable sites close to metropolitan areas is compounded by urban sprawl and persistent opposition from citizen and environmental groups. The rapid increase in problems and the costs associated with transporting refuse for long distances now make it prudent to consider sites that were previously unacceptable because they failed to meet certain geologic and hydrologic critera. As of January 1975, Illinois had 2,040 waste disposal sites recorded with the Illinois State Environmental Protection Agency. Since 1965, the management of refuse disposal in Illinois has greatly improved, owing to passage of the Illinois Refuse Disposal Act, which assigned the regulation of solid waste disposal to the Department of Public Health. More comprehensive regulation was provided in 1970 with the creation of the Environmental Protection Agency by passage of the Environmental Protection Act (HB3788). Regulations were passed that were designed to insure that solid waste disposal facilities are located at such sites and operated in such a manner as will protect the physical environment and public health. These regulations have been enforced for the past 10 years. During this time, the Illinois State Geological Survey has assisted the regulatory agencies by evaluating the hydrogeologic conditions at proposed or operating waste disposal sites. During the past 8 years, the Survey has appraised at about 100 sites annually the conditions relative to pollution hazard. Some sites were not approved for geologic reasons, including locations in floodplains or gravel pits, on fractured rock over aquifers, on steep grades, or in areas of special environmental significance. Other sites were approved but were never put into operation because of persistent opposition from citizen and environmental groups or for other reasons.

The future of landfill disposal is clear. Acceptable disposal sites will be difficult to find, their location will be approved only after certain geologic and hydrologic criteria are met, and greater care will be required in their operation. The relative unavailability of geologically acceptable sites in close proximity to metropolitan areas and the rapidly escalating costs associated with transportation of waste materials across long distances now make it economically feasible to consider physically modifying geologically unacceptable sites that may be ideal in other respects. The Illinois State Geological Survey has conducted extensive studies of the movements of pollutants through various geologic strata and in a variety of hydrologic settings at several landfill sites in northeastern Illinois (Hughes et al., 1971). Cartwright and McComas (1968) also conducted geophysical investigations at the same sites. The above studies, and others by Apgar and Langmuir (1971) and Emrich (1972), have indicated that pollutants in leachate can be detected at variable distances from a landfill, depending on the clay content of the soil or the hydraulic conductivity of the soil strata. It has therefore been suggested that a clay liner in the bottom of previously unacceptable sites, such as gravel pits or old quarries, could make them acceptable for disposal of municipal and/or industrial wastes. However, no sound evidence existed to indicate how thick such a layer must be or what types of clay minerals were best suited for removal of toxic metals in the presence of municipal leachate.

This paper reports the results of a study (1) to investigate and evaluate the attenuating properties of several clay minerals for the pollutants contained in leachates from municipal solid waste, and (2) to determine the capacity of the two major clay mineral types for removing the heavy metals -- Cr, Cu, Pb, Cd, Hg, As, Se, and Zn -- from solution and the effect municipal leachates have on this capacity at various pH values. The study was also designed to provide insight into the mechanisms responsible for attenuation of heavy metals as well as to evaluate the potential use of clay minerals as liners for waste disposal sites. Such liners would be used to prevent or mitigate pollution of ground and surface waters by liquid effluents.

It is clear that, based on their intrinsic properties alone, municipal leachates are noxious waste streams that pose a potential threat to public health (Hanks, 1967; Peterson, 1974). To assess the magnitude of the pollution hazard of such a stream is a difficult problem and was the subject of the U. S. Environmental Protection Agency (1973) decision model for screening, selecting, and ranking hazardous wastes streams. Use of the priority ranking formulation requires evaluation of the "critical product" (pollution hazard). At present, no actual waste-stream data for municipal leachates is available. Therefore, one goal of this study was to provide waste-stream data that could be used to determine the mobility index of several of the major pollutants found in municipal leachates that had passed through simulated clay mineral landfill liners. The mobility index thus derived could be used to compute the pollution hazard for most of the chemical constituents found in municipal leachate.

This report is presented in separate chapters that describe different aspects of the work that was performed. For the convenience of the reader, each chapter includes its own abstract. The column leaching studies (Sections 5 and 6) used "natural" landfill leachate as described in the Experimental section (Section 4). Sections 7 through 11 report equilibrium adsorption "batch" studies using small amounts of clays mixed with aqueous solutions of metal salts and landfill leachates that had been "spiked" with metal salts. The results of these investigations will also find application in the land disposal of industrial and energy production wastes.

SECTION 2

CONCLUSIONS

The results from the column leaching and adsorption studies have yielded complementary data that have allowed us to make predictions as to the expected magnitude of the reduction in concentration or attenuation in soil for most of the common chemical constituents found in landfill leachates. The data also indicate that several mechanisms may be responsible for attenuation of the various pollutants under differing environmental conditions.

Strong evidence is presented supporting the conclusion that the cation exchange capacity is the principal chemical property of a clay mineral to effect attenuation. Of the three clays used in this study, montmorillonite was found to have the highest attenuation capability, followed by illite and then kaolinite. This order was concluded to be a result of their respective cation exchange capacities.

The pH of the leachate was found to significantly affect the amount of attenuation. It was concluded that the heavy metal cations -- Pb, Cd, Cu, Cr(III), Hg, and Zn -- were attenuated primarily by an exchange-adsorption mechanism which was affected by pH and competition from other cations. However, at pH values between 5 and 6, a large increase in removal can be expected due to increased adsorption of metal complex ions and to formation of insoluble heavy metal hydroxide and carbonate compounds. It was therefore concluded that at high pH the primary mechanism of attenuation for these ions was precipitation. The effect of pH on the attenuation of the heavy metal anions Cr(VI), As, and Se was found to be the opposite of the cations and it was concluded that precipitation was not an important attenuation mechanism. Rather, the adsorption of the anions was found to correlate well with the distribution of certain ionic species in solution. It was concluded that $HCrO_4^-$ was the species adsorbing in this study, since Cr(VI) adsorption became zero as the pH was raised to 8.4, corresponding to the disappearance of $HCrO_4^-$ from solution in favor of the $CrO_4^=$ ion. The adsorption of Cr(VI) was also found to start to decrease as the pH was lowered past 2, corresponding to the decrease in $HCrO_4^-$ ion in favor of H_2CrO_4. Likewise, As and Se adsorption were also found to correspond to the distribution of $H_2AsO_4^-$ and $HSeO_3^-$ species in solution. These results led to the conclusion that the principal attenuation mechanism for the heavy metal anions was adsorption of the monovalent species from solution. It was also concluded that at higher pH values the heavy metal anions would be significantly more mobile than the cations.

The relative mobilities of the heavy metals, as determined from equilibrium adsorption data from pure solutions of the metals at pH 5, were:

$$Cr(III) < Cu < Pb < Zn < Cd < As(V) < As(III) < Se < Cr(VI)$$

The cationic heavy metals are generally adsorbed to a greater degree than are the anionic heavy metals. However, this ranking is dependent on pH and ionic competition and therefore changes somewhat in different leachates.

A significant point shown in the ranking is the importance of the valence state of an element to the amount of that element removed from solution by clay minerals. Cr(III) species were removed to a much greater extent than Cr(VI), and more As(V) was removed than As(III). These data suggested that safer disposal of certain elements may be achieved if the element were converted to the form most strongly attenuated prior to disposal.

The formation of Pb and Cd organic complexes in leachates was measured, and their effect was determined to be of secondary importance to adsorption and precipitation. This seemed to be due to competition from high concentrations of other cations present in leachates. Due to the complex interactions between inorganic, organic, and volatile forms of Hg, the mobility and relative importance of organic Hg complexes could not be accurately assessed.

The results of this study have led to the conclusion that passage of leachate through a Ca-saturated clay material will result in high attenuation of the heavy metals; in moderate attenuation of K, NH_4, Mg, and Si; and in relatively low attenuation of Cl, Na, and water-soluble organic compounds (COD). It was further concluded that the oxidation-reduction potential of the leachate controlled the attenuation of Fe and Mn. Under strongly anaerobic conditions, Fe and Mn will probably not be attenuated and may even elute in substantial concentrations due to the dissolution of oxide coatings on the clay surfaces. However, under mildly anaerobic conditions, substantial attenuation can occur.

Substantial concentrations of Ca were eluted from the columns. Since a very highly significant linear regression ($r = 0.97$) was obtained for the amount of Ca eluted versus the cation exchange capacity of the clay, and since the sum of the amount of K, NH_4, Na, and Mg removed from the leachate agreed within about 3% with the amount of Ca eluted, it was concluded that Ca elution was due to exchange with the other cations present in the leachate. It was also concluded that this Ca elution observed in the laboratory experiment corresponded to the "hardness halo" effect observed in field monitoring wells around sanitary landfill sites.

Significant reductions in hydraulic conductivity were observed when landfill leachate was passed through the columns. It was concluded that microbial action is primarily responsible for the observed reductions and that hydraulic activity of clay-sand liners placed in the bottom of a landfill will decrease after a period of leaching with municipal effluent. It was further concluded that montmorillonite clays will decrease in permeability to a greater extent than the other clays. This was assumed to be due to its tendency to swell to a much greater extent than other types of clay.

A pollution hazard ranking system was developed. Using this system, it was concluded that NH_4^+ was a 30 times greater pollution hazard than any other constituent found in the DuPage leachate. It was also concluded that in a fresh, young leachate, COD or Fe most likely would present the highest pollution hazard and that the characteristics of each leachate and earth material must be considered when evaluating their potential for pollution. The well known variability in composition of municipal landfill leachates (Garland and Mosher, 1975) and the difficulty in predicting leachate composition before landfilling is begun will make it difficult to apply this hazard-ranking system. Nevertheless, the ranking system has the advantage of quantifying the expected pollution hazard of a given leachate and allows comparisons of the pollution hazards of one leachate with another. The ranking system also aids regulators, landfill designers, and researchers by focusing attention on those chemical constituents in the leachate with the highest potential for serious pollution.

The mobility of a given leachate constituent, and hence the thickness of a clay liner necessary to attenuate the constituent, depends to a large degree on the element and the form of the element, the adsorption capacity of the earth material, the cations present initially on the exchange complex, the chemical composition of the leachate, and the pH of the leachate. The adsorption capacity of the clay minerals and the reversible nature of exchange-adsorption reactions have important environmental consequences. Industrial wastes containing heavy metals placed in sanitary landfills could alter the ionic composition and/or pH of the leachate. A change in pH may release large amounts of potentially toxic heavy metals into the aqueous phase, especially in places where precipitates may have accumulated. Other ions in the waste compete with the heavy metals and may exchange with them, thus allowing metal ions to come into solution. These multiple interactions must be considered when a disposal site is designed and when the environmental impact of adding heavy-metal wastes to municipal landfills is assessed.

SECTION 3

RECOMMENDATIONS

This study dealt specifically with attenuation of the inorganic constituents of leachate, but, because leachates contain high concentrations of organic compounds, also needed is a laboratory investigation dealing with the attenuation of the specific organic compounds in leachate. The results of our study, using COD as an indicator of organic-compound movement, showed poor attenuation of organics. At the same time, the pollution hazard index indicates that the organic fraction of leachate poses a serious pollution hazard, especially for young leachates. It is therefore recommended that an attenuation study be initiated, involving a comprehensive organic analysis to determine removal of specific organics by passage through clay liners and/or soils.

The results of this study also illustrated the important role that the pH of the leachate or waste stream plays in pollutant removal by clay minerals. It is therefore recommended that, in conjunction with the organic removal studies, further studies be carried out to determine techniques which will allow the pH to be manipulated to enhance and economically optimize pollutant (organic and inorganic) removal by earth materials. Also, landfill disposal of anionic forms of heavy metals such as Cr(VI), As, and Se should be closely scrutinized because of their relatively high mobility and the fact that manipulation of pH conditions to enhance removal of cationic heavy metals such as Pb, Cd, Zn, Cu, and Cr(III) may actually increase the mobility of the anionic metal ions.

Due to the relatively high toxicity of Hg and the complex interactions between inorganic, organic, and volatile forms of the element, much more research is necessary to determine the environmental impact of Hg in landfill environments. In conjunction with the study of Hg, Pt has also been reported to be methylated in aquatic systems, thus establishing a previously unknown mechanism of transfer. The major source of potential redistribution of complexed forms of Pt is expected to come from the disposal into landfills of spent catalysts from catalytic-converter-equipped automobiles. Thus, it is recommended that Hg and Pt be studied to quantitatively determine the adsorption capacity of clays and soils for the inorganic and organic forms of Hg and Pt. It is also important to determine the magnitude and role of microorganisms in the methylation of Hg and Pt to volatile forms under the conditions found in municipal landfills.

A major task still before us is the utilization of quantitative soil chemistry data to make predictions of pollutant migration beneath landfills.

It is therefore recommended that further studies be carried out that involve a cooperative effort between soil chemists, groundwater hydrologists, and modelers for the computer implementation of the prediction process and to identify possible gaps in knowledge that may still bar the successful prediction of long-term pollutant migration from disposal sites.

SECTION 4

EXPERIMENTAL

The clays used in this study were the purified clay minerals kaolinite (1:1 lattice type), montmorillonite (2:1 expanding lattice), and illite (2:1 nonexpanding lattice, mica type). These clay minerals were chosen for study because they are the most common clay minerals in earth materials that would be used individually or in combinations for landfill sites. Earth materials containing one or more of these clay minerals can generally be obtained locally for landfill liners.

The clays were brought to the laboratory, where they were crushed, ground, and purified by sedimentation techniques to obtain the <2 µm particle fraction that contained essentially pure clay minerals. Chemical analyses of the three clays are given in Table 1. Details of the methods used and results of X-ray diffraction analyses of the clays are given in the appendix. The predominantly Ca-saturated, <2 µm fractions of the clays were then used in the column leaching and heavy metal adsorption studies.

The municipal landfill-leachates used in this study were collected from the DuPage County landfill (well MM 63) and from the monitoring well located on the Blackwell Forest Preserve landfill. The details of the site descriptions and well locations are given by Hughes et al. (1971). The leachate was collected by using a tubing pump and large plastic containers that were equipped with valves to allow continuous purging of high-purity CO_2 or argon gas to maintain anaerobic conditions. The DuPage leachate collected initially for use in the column leaching study was stored under argon. Both the DuPage and Blackwell leachates collected at a later date for use in the heavy metal adsorption studies were stored under CO_2. Purging with CO_2, a naturally occurring landfill gas, was found to be a more satisfactory method than argon purging since it permitted the leachates to be stored in the laboratory for longer periods of time without significant changes in pH. The leachate used in the column study was collected with a tubing pump and was split into two 53-gallon plastic closed-head drums. One drum was taken to the Argonne National Laboratories and sterilized by gamma ray irradiation using a cobalt source which gave a dose of 3.36×10^6 rad at the center of the drum. Both the sterile and natural drums were stored under refrigeration with the temperature maintained at 3 to 5° C. The drum containing the microbially active leachate was stored with argon purged over the top of the leachate, while the sterilized drum was stored over a 12% ethylene oxide/88% freon gas mixture which maintained both sterility and an anaerobic environment. Mercuric nitrate salt was later added to the drum (Table 2) to maintain sterility. Plate counts were performed on both leachate drums using potato dextrose

TABLE 1. CHEMICAL CHARACTERIZATION OF THE CLAY MINERALS USED IN ATTENUATION STUDIES OF LEACHATE POLLUTANTS

Element	Kaolinite (Pike County, Illinois) (ppm)		Montmorillonite (American Colloid Co. southern bentonite) (ppm)		Illite (Minerva Co. Mine) (ppm)	
	Exch.*	Total	Exch.*	Total	Exch.*	Total
Ca	2,592.	3,700	13,120.	22,300	5,248	23,350.
Mg	76.8	1,800	680.	25,500	800.	10,430.
Na	43.2	929	24.0	178	115.2	1,050.
K	87.2	8,200	240.	1,100	800.	56,270.
NH_4	13.0	40	43.	38	50.	62.5
Fe	<2.0	6,600	<2.0	25,500	<2.0	28,730.
Mn	0.06	29	0.02	25	0.37	<390.
Pb	<2.0	46	<2.0	<15	<2.0	93.8
Cd	<0.2	<3	<0.2	<3	<0.3	18.8
Zn	0.80	20	1.00	40	2.5	37.5
B	-	46	-	3	-	43.8
Al	-	221,800	-	95,600	-	130,100.
Si	-	217,700	-	284,800	-	226,500.
Ti	-	14,700	-	1,300	-	4,010.
Carbon (%)						
Total		0.54		0.93		2.19
Organic		0.51		0.92		1.81
Inorganic		0.03		0.01		0.38
CEC (meq/100g)		15.1		79.5		20.5
Surface area (m^2/g)		34.2		86.0		64.6

*Exchangeable

TABLE 2. SUMMARY OF CHEMICAL CHARACTERISTICS OF LANDFILL LEACHATES

Component	Range of all values given by Garland and Mosher (1975) (mg/l)	Blackwell Forest Preserve leachate (Hughes, 1971b) (mg/l)	DuPage leachate used in sorption study (mg/l)	DuPage leachate used in column study (mg/l)	
				Natural	Sterile
COD	40 - 89,520	39,680.	1,362.	1,340.	10,603.*
BOD	9 - 54,610	54,610.	-	-	-
TOC	256 - 28,000	-	-	-	-
Organic acids	-	-	333.	333.	290.
Carbonyls as acetophenone	-	-	57.6	57.6	90.1
Carbohydrates as dextrose	-	-	12.	12.	11.
pH	4 - 9	7.10	6.79	6.9	7.2
Eh (m.v.)	-	-180.	-155.	+7.	+75.
TS	0 - 59,200	-	-	-	-
TDS	0 - 42,276	19,144.	5,910.	-	-
TSS	6 - 2,685	-	-	-	-
E.C. (mmhos/cm)	3 - 17	10.90	7.20	10.20	10.42
Alkalinity ($CaCO_3$)	0 - 20,850	3,255.	4,220.	-	-
Hardness ($CaCO_3$)	0 - 22,800	7,830.	1,100.	-	-
Total P	0 - 154	6.	<0.1	<0.1	<0.1
Ortho P	6 - 85	-	-	-	-
NH_4-N	0 - 1,106	-	809.	862.	773.
NO_3+NO_2-N	0 - 1,300	1.70	-	-	-
Al	-	2.20	<0.1	<0.1	<0.1
As	-	4.31	0.11	0.11	0.14
B	-	-	33.	29.9	28.5
Ca	5 - 4,080	-	49.	46.8	43.2
Cl	34 - 2,800	1,697.	1,070.	3,484.	3,311.
Na	0 - 7,700	900.	822.	748.	744.
K	3 - 3,770	-	516.	501.	491.
Sulfate	1 - 1,826	680.	<0.01	<0.01	<0.01
Mn	0 - 1,400	1.66	<0.1	<0.1	<0.1
Mg	16 - 15,600	-	204.	233.	230.
Fe	0 - 5,500	5,500.	4.40	4.2	3.0
Cr	-	0.20	<0.1	<0.1	<0.1
Hg	-	-	0.0008	0.0008	0.87*
Ni	-	-	0.3	0.3	0.3
Si	-	-	15.1	14.9	15.0
Zn	0 - 1,000	-	0.03	18.8	16.3
Cu	0 - 10	0.05	<0.1	<0.1	<0.1
Cd	0 - 17	<0.05	<0.01	1.95	1.88
Pb	0 - 5	-	<0.1	4.46	4.26

*Added as a result of sterilization maintenance agar media. No growth occurred on plates inoculated with the sterilized leachate while active growth of microbial colonies was observed on plates inoculated with the natural leachate, thus indicating that sterility had been achieved.

The results of chemical analysis of the leachates are presented in Table 2. Chemical procedures used are given in the appendix. For comparison, Table 2 also contains a summary of the range of leachate characteristics found for more than 20 other leachates as given by Garland and Mosher (1975). It is useful to note that the two leachates used in this study have widely different chemical compositions. The DuPage leachate is approximately 15 years old and has a lower total salt, phosphate, and sulfate content than the Blackwell. In addition, the organic matter of the DuPage leachate consists mainly of microbially resistant compounds, which have been found to be more mobile in soils than are biodegradable compounds (Hughes et al., 1971, Gowler, 1970). The Blackwell leachate, on the other hand, is younger and ranks among the most concentrated ever reported, especially with regard to BOD and Fe.

The laboratory apparatus used in the leaching study consisted of laboratory columns containing mixtures of clay minerals and washed quartz sand through which leachate was passed. A diagram of the column apparatus design appears in Figure 1. The columns and apparatus were constructed to simulate the slow (<2 pore volumes per month), saturated, anaerobic flow of leachate as it is thought to occur at the bottom of a landfill.

$$\text{Pore Volume} \cong \left[1 - \left(\frac{\text{Bulk Density}}{\text{Particle Density}}\right)\right] \times \text{Volume of Column} \qquad \{1\}$$

The entire column leaching system was maintained under an argon atmosphere to maintain anaerobic conditions. A tubing pump lifted the leachate to a 5-gallon plastic carboy which acted as both a constant head device (Marriot bottle) and a temperature equilibration reservoir. The leachate was then passed through the columns and the effluents were collected in graduated cylinders, which also allowed measurement of the flow rates. The outflow tube was maintained above the top of the columns to insure saturated flow. The level of the outflow tube was moved either up or down to maintain relatively constant flow rates throughout the experiment.

The columns were constructed of 2-inch acrylic tubing, to which manometer outlets were fitted vertically on the column at five locations. To simulate field conditions, the leachate containers and columns were either painted black or masked with black tape to prevent growth of organisms, such as algae or photosynthetic bacteria, which are not indigenous to deep refuse leachate.

The sand grains were coated with the clays, according to the methods given by Grim and Cuthbert (1945). The clay minerals and sand were then uniformly packed in the columns to a depth of 40 cm, except for the 32% and 64% montmorillonite columns, which were 30 cm thick. The columns were packed to bulk densities approximating those of naturally occurring glacial tills (~1.8 g/cc; Manger, 1963). Table 3 gives some chemical and physical properties of the column contents. The hydraulic conductivities for each particular

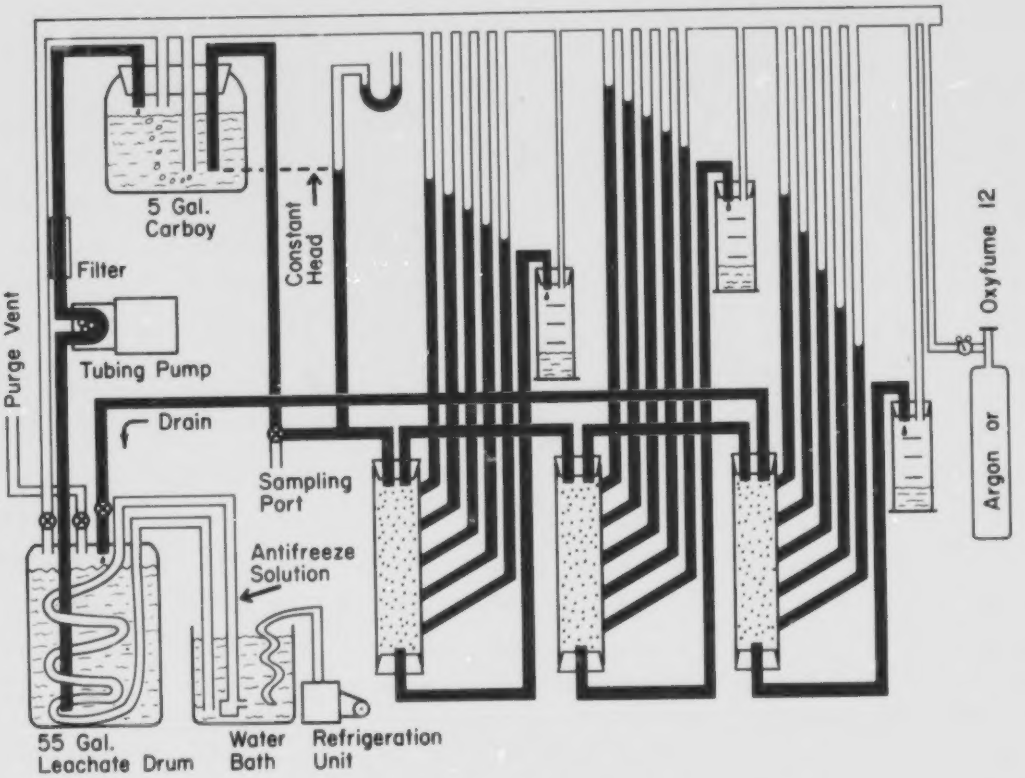
5 Gal.
Carboy
Constant
Head
Filter
Purge Vent
Tubing Pump
Drain
Sampling
Port
Antifreeze
Solution
55 Gal.
Leachate Drum
Water
Bath
Refrigeration
Unit
Oxyfume 12
Argon or

Figure 1. Diagram of column apparatus used in leachate study.

TABLE 3. DESIGN OF EXPERIMENT AND SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE COLUMN CONTENTS

Natural Leachate Treatment	Cation Exchange Capacity (meq./100g)		Bulk density (g/cc)		Initial hydraulic conductivity (cm/sec)	
	Set A*	Set B†	Set A	Set B	Set A	Set B
100 Sand	0.0	.1	1.71	1.71	$1.27.10^{-3}$	$1.80.10^{-3}$
2 M††	1.4	2.3	1.71	1.72	$9.45.10^{-4}$	$7.93.10^{-4}$
4 M	3.2	4.3	1.77	1.74	$4.34.10^{-4}$	$3.47.10^{-4}$
8 M	7.3	7.2	1.79	1.78	$4.70.10^{-4}$	$2.61.10^{-4}$
16 M	11.9	12.1	1.87	1.86	$1.22.10^{-5}$	$1.44.10^{-5}$
32 M	26.8	24.0	1.55	1.52	$1.27.10^{-6}$	$2.17.10^{-6}$
64 M	56.2	55.5	1.23	1.11	$3.05.10^{-7}$	$6.83.10^{-7}$
2 K††	0.7	0.4	1.68	1.70	$7.44.10^{-4}$	$4.53.10^{-4}$
4 K	1.1	0.8	1.76	1.74	$4.78.10^{-5}$	$2.76.10^{-5}$
8 K	1.5	1.4	1.80	1.77	$9.90.10^{-4}$	$8.25.10^{-4}$
16 K	1.8	2.5	1.87	1.90	$2.86.10^{-5}$	$1.92.10^{-6}$
32 K	3.8	3.4	1.66	1.55	$2.40.10^{-6}$	$4.81.10^{-6}$
64 K	9.6	8.5	1.22	1.32	$5.45.10^{-7}$	$4.57.10^{-7}$
4 I††	0.8	0.9	1.80	1.81	$8.17.10^{-4}$	$7.16.10^{-4}$
16 I	3.5	3.2	1.83	1.91	$2.68.10^{-5}$	$2.19.10^{-5}$
8K + 8I	2.4	2.3	1.90	1.98	$1.48.10^{-6}$	$1.68.10^{-6}$
8M + 8K + 8I	8.8	8.5	1.64	1.69	$8.08.10^{-6}$	$9.43.10^{-6}$

*Set A - Natural leachate

†Set B - Sterile leachate

††M = Montmorillonite, I = Illite, K = Kaolinite

clay content and bulk density agree with those given by Todd (1959) for natural materials. The experimental design used in the study is also shown in Table 3, which gives the percentages of clay mineral(s) in each column (to which pure quartz sand was added to total 100%). The experimental design includes a complete geometric progression of clay percentages from 2% to 64% kaolinite and montmorillonite and two mixtures of clays as given in Table 3. A 100% sand column was also included. Only 4 and 16 percentages of illite were included because kaolinite and illite have very similar cation exchange and lattice expansion properties, and thus a complete geometric array for illite was not considered necessary.

After the leachate and the column contents were characterized, the leachate was passed through the columns for periods of between 6 and 10 months, depending on the hydraulic conductivity of the individual column. The hydraulic conductivity (K) was computed using the relationship:

$$K = \frac{QdL}{AdH} \tag{2}$$

where Q = flow rate in cm^3/sec
A = cross sectional area of column in cm^2
dL = length of the column in cm
dH = head of water in cm.

During this time effluents from each column were collected periodically and measurements were made for Na, K, Ca, Mg, Al, Zn, Pb, Cd, Hg, Fe, Mn, NH_4, B, Si, Cl, chemical oxygen demand (COD), Eh, pH, and hydraulic conductivity. Finally, after approximately 15 pore volumes were leached, the clay mineral columns were sectioned and the contents analyzed to determine the vertical distribution of chemical constituents in each column.

Duplicate sets of columns were used in the experiment; one set of columns was leached with natural effluent, another with sterilized effluent. The sterilized treatment was used to determine how gross biological activity might affect hydraulic conductivity of leachate through clay minerals used as liners. The results of the experiment were statistically analyzed using the paired t statistic to determine if there were significant differences in the attenuation of each chemical constituent between sterile and natural leachate and between clay mineral types. Linear regression and moving average analysis were also performed on the column effluent data to determine relationships between hydraulic conductivity, attenuation, and clay mineral properties.

In addition to the column leaching study, a series of separate equilibrium studies on the capacity of clays to adsorb eight potentially hazardous elements -- Pb, Cd, Zn, Cu, Cr, As, Se, and Hg -- were performed. From these studies, adsorption isotherms for kaolinite and montmorillonite were constructed to determine the adsorption capacities as a function of concentration, pH, and ionic competition. The details of the experimental procedures used for each element are included in the section of the report dealing with that particular element.

SECTION 5

COLUMN LEACHING STUDY[1]

ABSTRACT

To evaluate the potential of clay minerals for attenuating the various chemical constituents of landfill leachate, leachate was collected by anaerobic techniques from the 15-year old DuPage County sanitary landfill near Chicago, Illinois, and passed through laboratory columns that contained various mixtures of calcium-saturated clays and washed quartz sand. The columns were constructed to simulate slow, saturated, anaerobic flow of leachate through earth materials outside the landfill. Manometers were placed in each column to measure any changes in permeability. Leachates were run through the columns for periods of up to 10 months, during which time effluents were periodically collected and analyzed for 16 chemical constituents. The column contents were then cut into sections and analyzed to determine the vertical distribution of chemical constituents in each column.

Chloride, Na, and water-soluble organic compounds (COD) were relatively unattenuated by passage through the clay columns; K, NH_4, Mg, Si, and Fe were moderately attenuated; and heavy metals, such as Pb, Cd, Hg, and Zn, were strongly attenuated by even small amounts of clay. Concentrations of Ca, B, and Mn in the column effluents increased markedly over the original leachate concentrations. The increase in Ca was due to cation exchange with ions in the leachate. The amount of Ca eluted from the columns was found, by mass balances, to agree within 3% with the sum of Na, K, NH_4, and Mg removed from solution. The Mn increase probably resulted from a reduction of the oxidized Mn on clay surfaces by the anaerobic leachate to more soluble ionic species.

Of the three clays used in the study, montmorillonite had the highest attenuation capability, followed by illite and then kaolinite. This order correlates well with the cation exchange capacities of the three clay minerals, which appear to be the dominant attenuation mechanism in these clays. The principal attenuation mechanism for the heavy metals Pb, Cd, Hg, and Zn was found to be precipitation, with resultant accumulation of the metals in the surface layers of the columns.

A ranking system was developed for evaluating the relative pollution hazard for municipal leachates. The new ranking method overcomes the problems and objections found in evaluation of the critical product parameter for

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[1] Authors: R. A. Griffin, N. F. Shimp, J. D. Steele, R. R. Ruch, W. A. White, and G. M. Hughes.

municipal leachates by a method previously proposed to the U. S. EPA for hazardous wastes.

Results of the study are applicable to the use of clay minerals as liners for sanitary landfills and to the disposal of industrial and power plant wastes in landfills and mines.

INTRODUCTION

The following results and discussion consider data from the columns leached with normal leachate and do not include results from the sterilized leachate. Details of the effect of sterile leachate on hydraulic conductivity and chemical constituent attenuation will be the subject of Section 6. However, for those chemical constituents for which no significant difference in attenuation between the normal and sterile leachate treatment was found, the results were pooled to give added statistical significance to analysis of clay-type effects. Those constituents for which no significant difference was observed were Ca, Mg, Na, K, NH_4, Pb, Hg, Zn, and Cd.

COLUMN LEACHING STUDIES

Hydraulic conductivity and bulk density measurements of the column contents are presented in Table 3. A wide range of hydraulic conductivities, with values in agreement with those expected under field conditions from similar materials (Todd, 1959), was observed. The relatively high bulk densities and slow flow rates used in this study closely simulate the conditions observed in the field, which lends credence to the extrapolation of the results and conclusions presented here to field applications using clay liners of similar composition.

Results of some column effluent analyses are shown in Figures 2 and 3 plotted as relative concentration versus pore fraction. Relative concentration is the ratio of the column effluent concentration divided by the influent concentration. Thus the "breakthrough" point for a given element is where the column effluent concentration equals the influent concentration and has a value of one. A pore volume of effluent is defined as the volume necessary to displace the volume of interstitial liquid in the pore spaces in the column. The pore fraction is then given as the cumulative volume of column effluent divided by the pore volume of the individual column.

Figures 2 and 3 illustrate the wide range of attenuation observed for several elements contained in the leachate as it passed through columns containing 2, 8, and 16% montmorillonite clay. The amount of reduction in concentration of a given element as it passes through the columns is reflected by the shift of the curves toward higher pore volumes. The results shown in Figure 2 for Cl, Na, NH_4, and K are qualitatively in excellent agreement with the results reported by Farquhar and Rovers (1975), who used soils in their tests. The attenuation order also follows the general order of cation replaceability given by Grim (1968).

Figure 3 illustrates the negative attenuation or elution of Ca from the columns. The relative concentrations greater than 1 indicate that Ca, and to

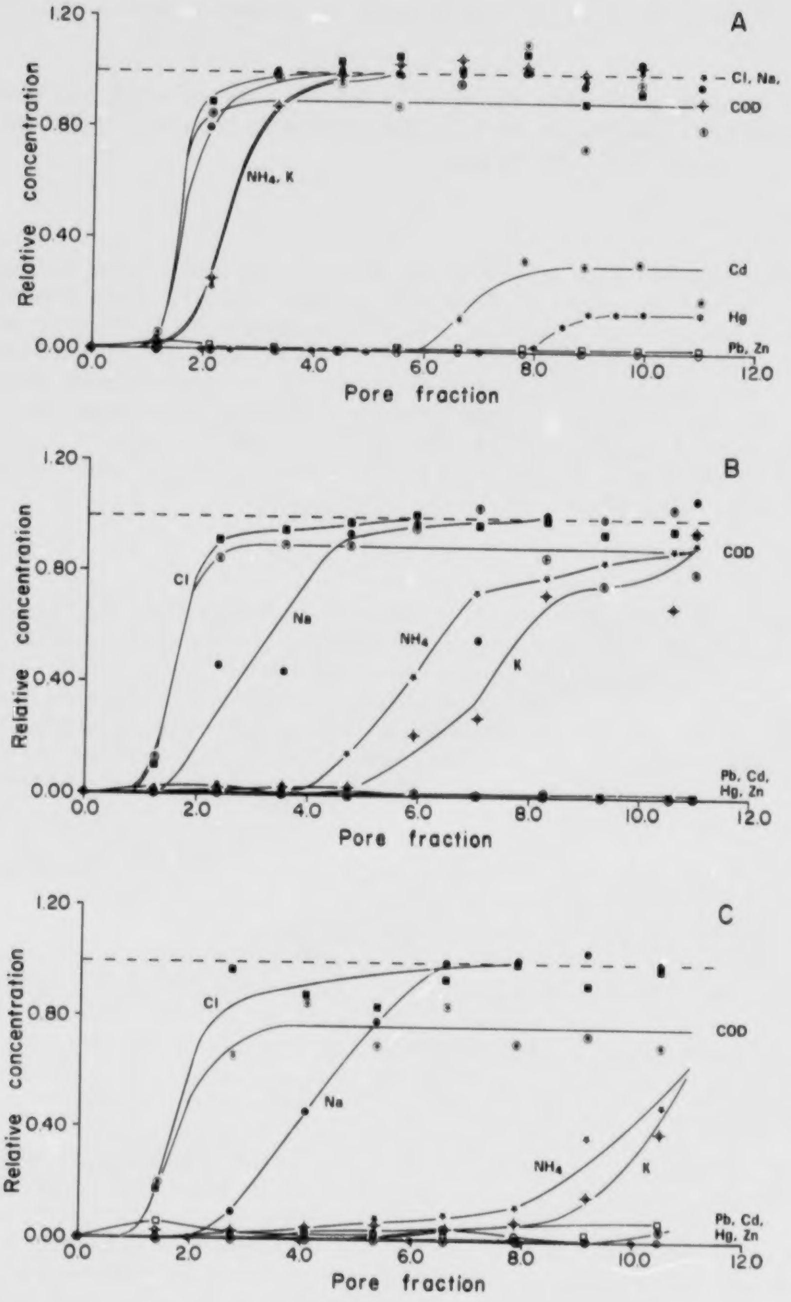

Figure 2. Relative column effluent concentrations for several elements as a function of pore fraction of leachate passed through columns containing (a) 2% montmorillonite, (b) 8% montmorillonite, and (c) 16% montmorillonite clay.

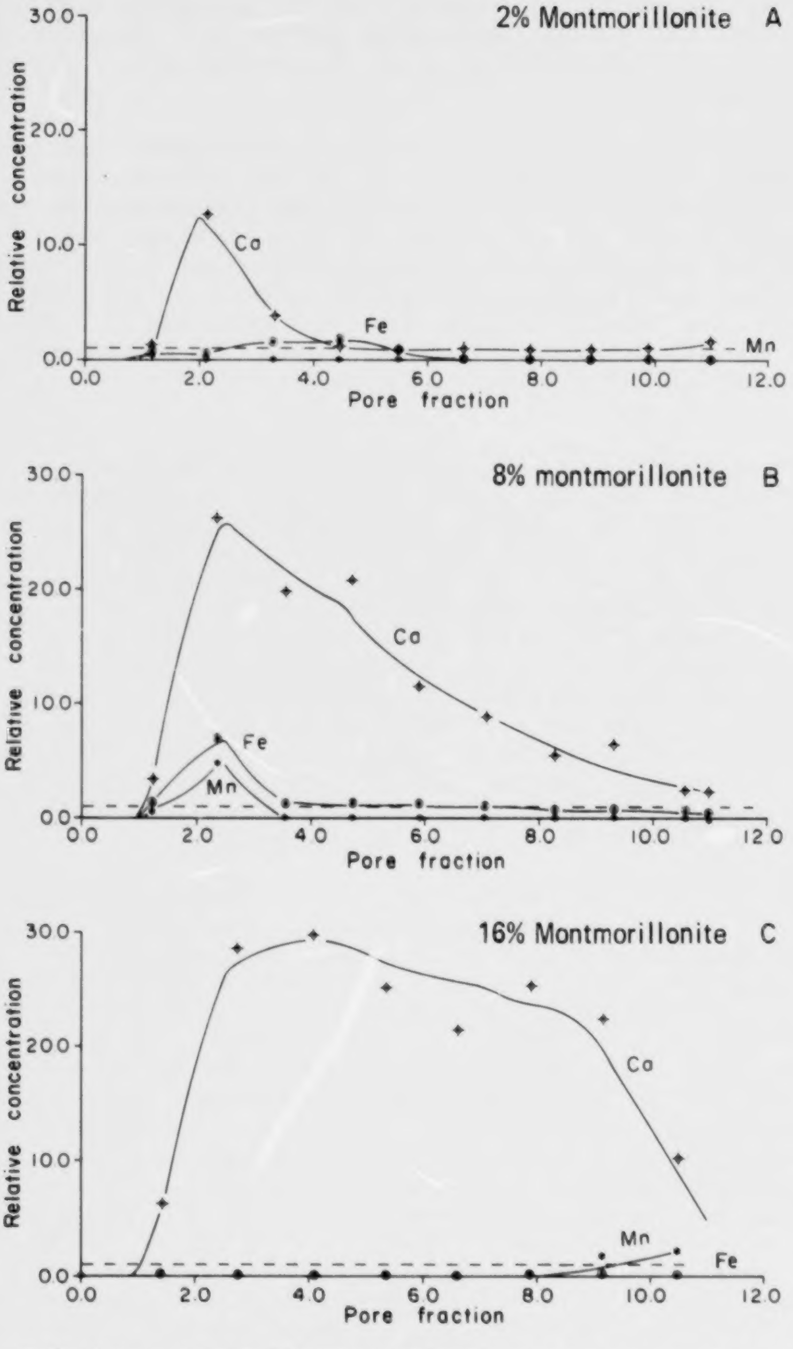

Figure 3. Relative column effluent concentrations for several elements as a function of pore fraction of leachate passed through columns containing (a) 2% montmorillonite, (b) 8% montmorillonite, and (c) 16% montmorillonite clay.

a lesser extent Fe and Mn, are eluting from the columns at much higher concentrations than the influent leachate at various pore fractions. The area under the Ca curves in Figure 3 increases in proportion to the percentage of clay in the column.

To quantify the observed attenuation, the area under each curve was integrated between pore fractions 1 and 11. The area between 0 and 1 pore fraction was not included because it was merely the displacement of the deionized water initially present in the column. The total area was that bounded by 10 pore volumes and relative concentrations between 0 and 1. The relative attenuation number (ATN) was then obtained by subtracting the area under the curve in each case from the total area and was expressed as a percentage. The ATN numbers are unique for each element and each clay and express the relative mobilities of each element through each particular clay or clay mixture column.

The attenuation number was computed for all columns and each chemical constituent studied. The mean attenuation number for each chemical constituent was used to rank the constituents according to their relative mobility through the clay columns and is reported in Table 4. The constituents Al, Cu, Ni, Cr, As, S, and PO_4 were found in such low concentrations in the DuPage leachate that no attenuation order could be determined. The results showed that greater amounts of the heavy metals Pb, Zn, Cd, and Hg than any other element were removed from leachate, yielding an average of about 97% attenuation for 10 pore volumes leached. The data for 2% montmorillonite (Fig. 2a) show that Cd and Hg were the most mobile of the heavy metals studied. Measurable amounts of Cd and Hg appeared in the effluents of the 2% clay column after about 6 pore volumes were leached. Only traces of Cd and Hg appeared in the effluents of the 8% and 16% clay treatments (Fig. 2b, 2c). Removals of Pb and Zn were very high in all columns.

Results obtained from chemical analysis of sectioned columns revealed large accumulations of all four heavy metals in the surface layers of each column, including the 100% sand column. These removals could be attributed to cation exchange replaceability, but a precipitation and/or filtration mechanism appears a more plausible cause. Precipitation could involve formation of heavy-metal hydroxides or carbonates, brought about by the relatively high pH found in the column effluents. The average pH of the influent leachate was 6.9, while the average pH of the column effluents rose to values of 7.3-7.9. The increase in pH could result in precipitation of the heavy metals from solution in the columns. The precipitation mechanism is given further credence by the measurements of the effluent concentrations from the sand columns, which have no cation exchange capacity and an average effluent pH of 7.8. No Pb and markedly reduced concentrations of Zn, Cd, and Hg eluted from the sand columns. These data, along with the high accumulations of the metals in the surface layers of the sand columns, indicate that precipitation of heavy-metal hydroxides and carbonates can be an important attenuation mechanism. This conclusion has been further verified by our equilibrium studies of the effect of pH on heavy-metal removal by clay reported in Sections 7, 8, 9, 10, and 11 of this report.

Filtration of particulate material in the leachate by the earth

TABLE 4. RANK OF CHEMICAL CONSTITUENTS IN MUNICIPAL LEACHATE ACCORDING TO THEIR RELATIVE MOBILITY THROUGH CLAY MINERAL COLUMNS

Chemical constituent	Mean attenuation number	Principal attenuation mechanism	Relative mobility
Pb	99.8	Precipitation/Exchange	Low
Zn	97.2	Precipitation/Exchange	
Cd	97.0	Precipitation/Exchange	
Hg	96.8	Precipitation/Exchange	
Fe	58.4	Oxidation-Reduction	Moderate
Si	54.7	--	
K	38.2	Cation Exchange	
NH_4	37.1	Cation Exchange	
Mg	29.3	Cation Exchange	
COD	21.3	Microbial Degradation	High
Na	15.4	Cation Exchange	
Cl	10.7	Dispersion	
B	-11.8	Artifact?	More Eluted Than Applied
Mn	-95.4	Elution from Clay	
Ca	-656.7	Exchanged from Clay	

materials is also a possible attenuation mechanism. Experiments in which the DuPage leachate was filtered through 0.45 μm pore size membranes indicated that only relatively small amounts of metals were retained on the membrane. It was therefore concluded that filtration was not an important attenuation mechanism for the heavy metals in this study but may be an important mechanism for many other leachates.

Moderate attenuation was observed for the leachate constituents Fe, Si, K, NH_4, and Mg, which had values ranging between 58.4% and 29.3% attenuation. Little attenuation was found for COD, Na, and Cl, values for which ranged between 21.3% and 10.7% attenuation. The elements Ca, Mn, and B were not attenuated by the clays, but, rather, were found in substantially higher concentrations in the column effluents than in the influent leachate.

To determine what mechanisms were responsible for the observed differences in attenuation for each leachate constituent, the effect of clay type was investigated. The mean attenuation obtained for each clay and chemical constituent is tabulated in Table 5. The results show that no significant difference in attenuation for the three clay minerals was observed for the heavy metals (Pb, Cd, Hg, Fe, and Zn) or for B or Cl. Illite and kaolinite attenuated Si significantly better than montmorillonite. Kaolinite was found to elute Mn in significantly higher amounts than either montmorillonite or illite. No significant difference in COD attenuation between montmorillonite and illite was found, and both attenuated COD significantly better than kaolinite. Montmorillonite was found to attenuate the cations Na, K, NH_4, and Mg and to elute Ca to a significantly greater degree than illite and kaolinite.

A precipitation mechanism for the four heavy metals (Pb, Cd, Hg, and Zn), as discussed above, is consistent with the fact that no differences in attenuation were found among the three clays. Because these four metals exist in solution as cations, a significant clay-type effect would be expected if cation exchange were the attenuation mechanism. No clay-type effect was observed, which is taken as additional evidence that the primary attenuation mechanism for these four heavy metals is precipitation.

To determine whether the higher attenuation of the cations Na, K, NH_4^+, and Mg and elution of Ca by montmorillonite was due to its higher cation exchange capacity, the attenuation numbers were plotted as a function of CEC for the three clay minerals. The results are shown in Figures 4 and 5. The very highly significant linear regression of attenuation numbers as a function of CEC led to the conclusion that the principal attenuation mechanism for Na, K, NH_4, and Mg was the cation exchange of these constituents for Ca.

Ca was the predominant exchangeable cation present on these clays at the beginning of leaching (Table 1). To further confirm that this mechanism was responsible, a mass balance for these five cations was computed for data presented in Figure 2. The sums of the amounts of Na, K, NH_4, and Mg removed from the leachate agreed within 3% with the amount of Ca eluted. Increases in the concentration of alkaline earth metals in groundwater preceding a leachate plume have been observed in the field during monitoring of the groundwater chemistry around landfill sites. Such increases, termed the "hardness

TABLE 5. MEAN ATTENUATION NUMBER (ATN) OF SOME CHEMICAL CONSTITUENTS FOUND IN MUNICIPAL LEACHATES FOR THREE CLAY MINERALS

Chemical constituent	Mean ATN			
	Montmorillonite	Illite	Kaolinite	All columns
Pb	99.6*	100.0	99.9	99.8
Zn	97.7	98.6	98.1	97.2
Cd	96.7	100.0	97.5	97.0
Hg	98.4	98.1	95.2	96.8
Fe	34.8	82.8	67.6	58.4
Si	39.2	81.6	71.2	54.7
K	58.9	31.0	23.2	38.2
NH_4	54.8	31.0	25.1	37.1
Mg	48.2	19.7	18.1	29.3
COD	24.6	23.2	16.2	21.3
Na	20.6	16.4	9.7	15.4
Cl	9.3	13.5	14.3	10.7
B	-16.1†	-12.8	-11.5	-11.8
Mn	-73.2	-6.4	-266.2	-95.4
Ca	-885.5	-233.3	-190.2	-656.7

*Underlined means are not significantly different (0.05).
†Minus numbers indicate elution.

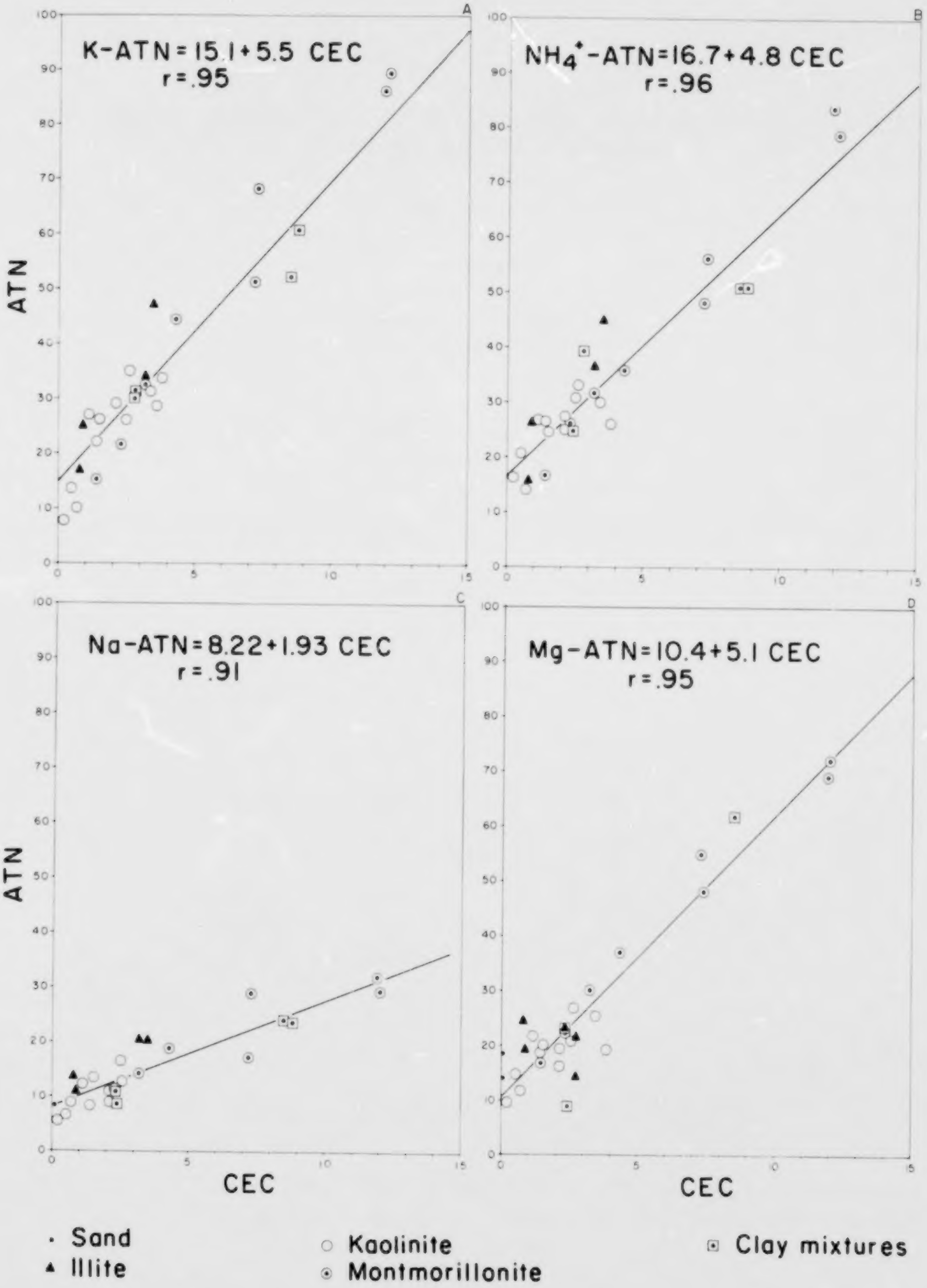

Figure 4. The attenuation number related to cation exchange capacity (a) K, (b) NH$_4^+$, (c) Na, and (d) Mg.

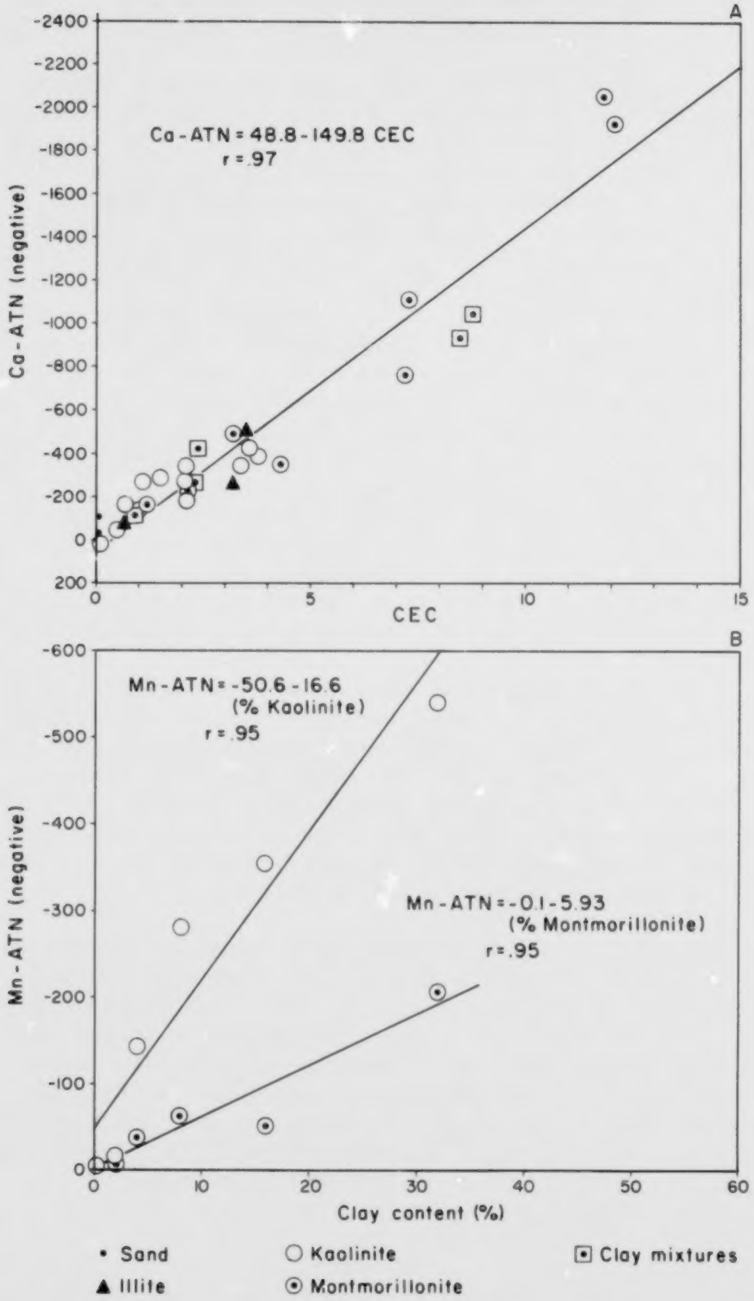

Figure 5. (a) Ca attenuation number related to cation exchange capacity.
(b) Mn attenuation number related to clay percentage.

halo," are likely due to the same mechanism responsible for the Ca elution from the columns in this study. This is discussed further in Section 6.

No significant linear regression of attenuation as a function of either CEC or clay percentage was obtained for Fe, Si, COD, Cl, B, or Mn, except for a very highly significant linear regression obtained for Mn elution and clay percentage. The results of the regression of Mn elution as the percentage of kaolinite and montmorillonite increased are presented in Figure 5b. No significant linear regression could be obtained with illitic clay because only two illite columns were used. The data illustrated in Figure 5b show that approximately three times as much Mn eluted from the kaolinite-containing columns as from the montmorillonite columns. The data presented in Table 1 indicate that kaolinite contains only slightly more total Mn than montmorillonite. However, surface Mn is three times more abundant on kaolinite than on montmorillonite and corresponds to the increased elution from the kaolinite columns. No correlation of Mn elution was observed with CEC, and the amounts of surface-extractable Mn correlate with the amounts eluted from the various columns. These facts, along with the anaerobic conditions in the columns, have led to the conclusion that Mn elution is due to the reduction of surface coatings of Mn compounds on the clays to more soluble reduced ionic species. The increase in Mn elution from kaolinite columns is proportional to, and apparently due to, the larger amount of Mn on the surface, where it is readily available for reduction and solubilization by the anaerobic leachate.

The behavior of Fe is similar to that of Mn; however, it is more sensitive than Mn to the oxidation potential in the leachate. During the early stages of leaching, Fe was also solubilized and eluted from the columns, as is shown in Figure 3. However, unlike Mn, Fe showed a net attenuation of 58.4% when the entire 10 pore volumes leached were considered. The results of this study, therefore, indicate that Fe may be either eluted or not attenuated by clay liners if the leachate is strongly anaerobic, or it may be strongly attenuated under weakly anaerobic conditions.

Other data from this study indicate that attenuation of COD was relatively low after passage of DuPage leachate through clay columns. This result is in agreement with those of Urioste (1971), who reported poor removal of COD when leachate was ponded on soils. The lack of a strong clay effect and of a significant correlation of attenuation of COD with either clay percentage or CEC indicate that the observed attenuation was probably the result of microbial degradation of the organic compounds. The fact that the leachate is relatively old probably accounts for the relatively low reduction in COD. It has only a small percentage of readily degradable organics and a low nutrient status, owing to the lack of PO_4 (Table 2).

Chloride attenuation was also relatively low, only 10.7%. This low attenuation is not surprising, because Cl is considered as a mobile non-interacting anion in soil systems. The low Cl attenuation was not a function of the type or amount of clay mineral present and is attributed to physical dispersion in the porous column media, with perhaps a small amount of interaction at anion exchange sites on the clay, or to other chemical reactions.

Since Cl is a negative ion, it would be attracted only by the positive charge at the edge of the clay minerals. Oxygen and OH are the negative ions of the lattice, and any other negative ion would have to be nearly the same size as the oxygen ion in order to coordinate with and continue or substitute for the oxygen. Because the chloride ion is about two and one half times the volume of the oxygen ion, it is too large to replace or coordinate with the oxygen and hydroxyl ions, although fluorine can do so because it is about the same size as the oxygen and hydroxyl ions.

No attenuation of B was observed in this study; rather, a small elution of boron from the columns took place throughout the leaching experiment. This may be interpreted as a slight solubilization of B from the clay minerals or sand in the columns. However, no effect of type or percentage of clay and no changes in elution with leaching time were found during the study. These facts have led to the conclusion that the B results may be an artifact of the experiment. It has been suggested that B may be dissolving from the borosilicate glass tubing used throughout the apparatus. More importantly, B may be solubilized from the spun glass wool used as a filter to keep sand and clay from migrating into each of the five manometers and the outflow tubing (Fig. 1). The high surface area of the spun glass and the neutral pH of the leachate make it plausible that the boron elution may be due to contamination. In any case, no attenuation of boron was observed in this study.

The results presented in Figure 4 and Table 5 permit the three clay minerals to be ranked, according to their overall attenuating ability for the chemical constituents found in municipal leachate, as follows:

montmorillonite > illite > kaolinite.

The montmorillonite used in this study has properties similar to those of smectites produced by weathering of micas, chlorites, and other crystalline minerals. The cation exchange capacity is lower than that for montmorillonite produced from weathering of volcanic ash and basaltic rocks.

The montmorillonite used produces clay material (e.g., Porter's Creek Clay) that have much higher permeabilities than those from Wyoming-type montmorillonite. Such high permeability should make this montmorillonite more useful than some other types of montmorillonite in making landfill liners in humid climates. With its high cation exchange capacity, it would adsorb more of the cations in the leachate than either illite or kaolinite. With its greater permeability, it allows more water to pass through the liner than do many other types of montmorillonite. The low permeabilities of other montmorillonite types would probably increase the hazard of lateral seepage from the sides of the landfill in humid climates.

Some sodium montmorillonites tend to shrink when sodium is exchanged for divalent and trivalent cations or when salt concentrations are high. This shrinkage sets up tension, which in turn produces cracks called syneresis cracks. Syneresis cracks were common in irrigation ditches in Colorado that were lined with sodium montmorillonite (personal communication, R. D. Dirmeyer, Jr., 1961). Shrinkage could be reduced considerably by using calcium montmorillonites and mixing them with other earth materials (e.g., 16 to 32% montmorillonite and 68 to 84% sand).

The kaolinite used in this study is a fine-grained material in which the crystallinity of the kaolinite crystals is poor. It has a high cation exchange capacity compared with other kaolinites. Well crystallized kaolinites with large crystals have a cation exchange capacity of 1 to 5 meq/100 g. The kaolinite used in this study would be better suited than most kaolinites for landfill liners. The permeability of this kaolinite is lower than that of well crystallized kaolinite with large crystals. The kaolinite in most sediments has a cation exchange capacity and permeability between those of the kaolinite used and the well crystallized kaolinites.

The illite used is similar in cation exchange capacity and permeability to the illite found in most sediments. The sediment from which the experimental illite was taken contained only one clay mineral -- the illite -- whereas most sediments that contain illite also contain other clay minerals.

It was concluded that the attenuation order was due principally to the cation exchange capacity of each of the three clays.

Attenuation of Leachate

During the period of time from collection of the leachate through the establishment of hydraulic equilibrium, the leachate was stored in a refrigerated (3 to 5° C) condition with either argon or sterilant gas being purged slowly over the top of each respective drum. Chemical analyses were performed weekly on the leachate to monitor possible changes in composition. As a result of this monitoring, it was determined that the COD of the sterile drum was steadily rising. It was determined that the active component of the sterilant gas, ethylene oxide, was able to react with the chloride ion present in the leachate which acted as a nucleophile to produce ethylene chlorohydrin (Rosenkranz and Wibdkowski, 1974). When it was discovered that the COD was rapidly rising, the use of the sterilant gas was discontinued. Argon was then used as the purge gas for both drums and mercuric nitrate salt was added to the sterile drum to maintain sterility. Further monitoring of both drums was continued at approximately 1 week intervals during the 10 month period during which leaching of the columns occurred. The COD values were found to remain constant at the value obtained when purging of sterilant gas was discontinued. The value reported in Table 2 for COD, and for all the other constituents, is the average of the 37 separate analyses performed during the 10 month period of leaching.

Determination of the attenuation of chloride and the other major components of DuPage leachate has been described in Section 5. The results of this study indicated that there was an average 6% greater attenuation of chloride in the columns leached with sterile leachate than those leached with the natural leachate. This greater attenuation is attributed to the reaction of chloride with the ethylene oxide to form ethylene chlorohydrin. Other than the slight increase in chloride attenuation, no other significant difference was apparently due to the increase in COD in the sterile leachate as compared to the natural leachate.

There were, however, other significant differences between the sterile and natural leachate treatments which were not attributed to the higher COD of the sterile leachate. Figure 6 illustrates the difference observed in Mn elution from the colums. It should be noted that a negative attenuation number indicates that more Mn eluted from the column than was present in the influent leachate. It can be seen that much higher levels of Mn were found in effluents from the columns leached with natural leachate. It was concluded in Section 5 that this elution was due to reduction of surface coatings of Mn oxides on the clays by the anaerobic leachates. This conclusion is further verified by the difference in Mn elution between the natural and sterile leachate treatment. This difference is attributed to the stronger anaerobic environment provided by the active microorganisms present in natural leachate. Inspection of the data in Table 2 shows that the average Eh (oxidation potential) reading of the natural leachate was 10 times lower than the sterile leachate, even though both were well in the anaerobic range (Eh readings less than 197 m.v. are considered to reflect anaerobic conditions). A similar result was obtained for Fe in that significantly (.05 level) greater mobility of Fe was found in columns leached with natural leachate as compared to those leached with sterile leachate. A mechanism similar to that for Mn is postulated as the reason for the observed differences between the natural and sterile leachate.

Those chemical constituents for which no significant difference in attenuation between the normal and sterile leachate was found were Ca, Mg, Na, K, NH_4, Pb, Hg, Zn, and Cd.

POLLUTION HAZARD OF LEACHATE

In addition to determining the relative mobilities of the various chemical constituents of leachate through clays (liner materials), their relative pollution hazard should be evaluated. Ranking wastes in terms of their existing or potential threats to public health and/or the environment has been the subject of the "Priority Ranking System" suggested for development by the U.S.-EPA (1973).

The priority ranking formula is:

$$R = \dot{Q}/CP \qquad \{3\}$$

where R = ranking factor,

Q = annual production quantity for the waste being ranked, and

CP = critical product for the waste being ranked.

A critical product is the lowest concentration at which any of the hazards of concern become manifest in a given environment, multiplied by an index representative of the waste's mobility into that environment. Thus, for a municipal leachate that would be discharged through a clay liner or soil into an aquifer used for drinking water, the toxicity factor could be the public water supply limits for the given element, and the mobility index could be the attenuation numbers derived above.

Evaluation of the critical product for municipal leachates moving through soils or clay liners by the U.S.-EPA (1973) formula proved to be awkward and unsatisfactory for several reasons. The first problem encountered

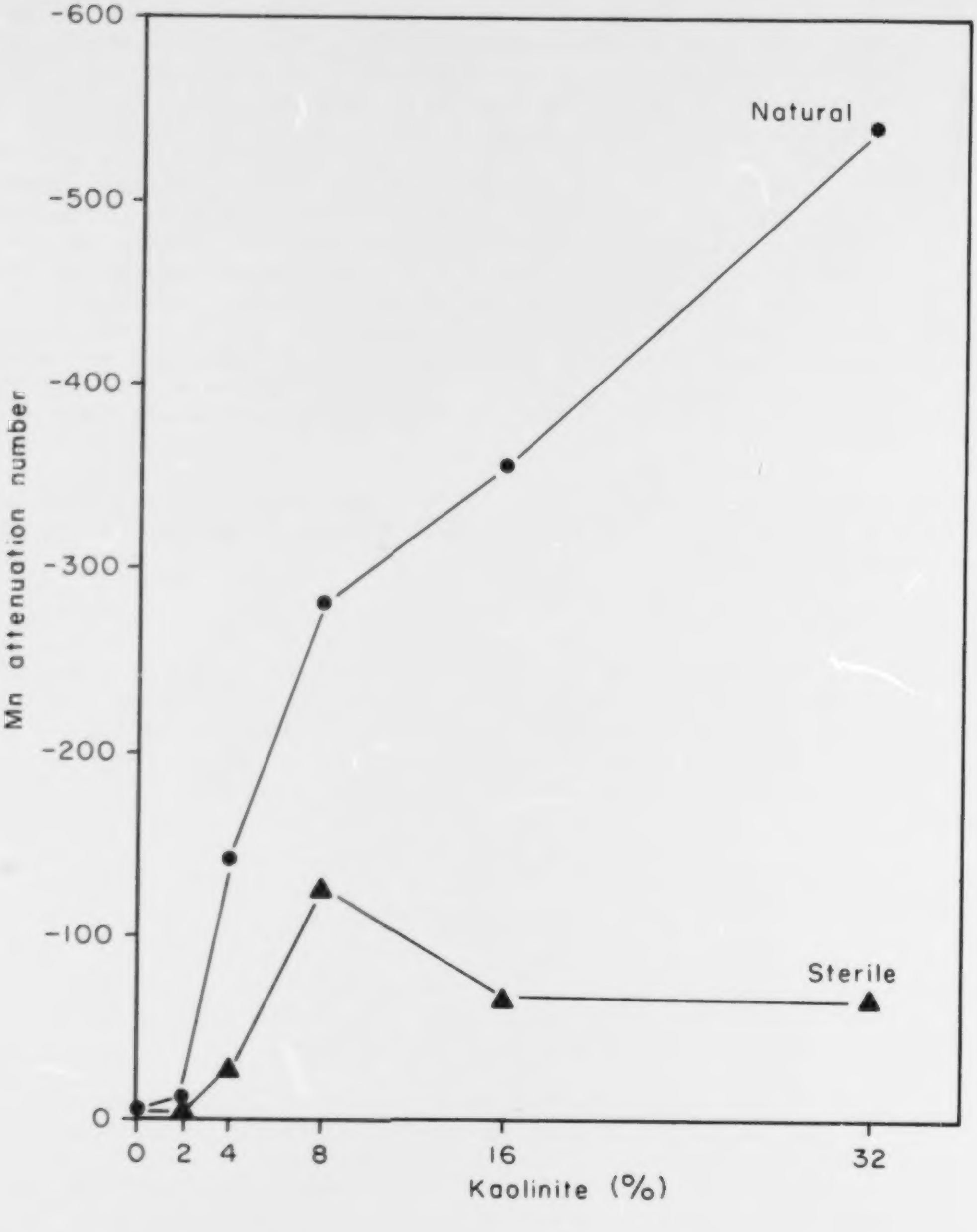

Figure 6. Manganese elution related to percentage of kaolinite leached with natural and sterile leachate.

was that negative attenuation numbers, such as those obtained for calcium, were not accounted for by the formula. A transformation of the data would be necessary to express the negative numbers in a manner that could be used in the CP formulation.

The second problem encountered was evaluation of the CP for the four heavy metals. An upper boundary on the attenuation number, such as the 100% removal, used to express the heavy metal removed from leachate is not allowed conceptually by the formula. Instead, what is required is the actual attenuation as determined by leaching until "breakthrough" of the particular element is achieved. For Pb, an estimated 300 pore volumes would have to be leached through an average column to achieve breakthrough. It was deemed impractical to actually measure the breakthrough of the heavy metals, and estimating their breakthrough required additional analytical data that could cause errors in estimating the pollution hazard.

A third problem with evaluating the pollution hazard by using the CP was that it was not specific for the waste being evaluated in that the concentration of the element of interest in the waste did not enter into the evaluation of the hazard. That this is a serious fault can be illustrated by simple examples: an element with a relatively high toxicity and mobility index could get a high hazard rating, even though only a trace was present in the waste; conversely, an element with a relatively low toxicity and mobility could receive a low hazard rating even though it was present in very high concentrations.

A fourth criticism of the CP rating was that it was conceptually illogical because large CP values indicated a low pollution hazard and, conversely, a very small number represented a very high hazard. It was considered more logical to express high pollution hazards as large numbers when a relative scale was used or when pollution potentials were evaluated.

To overcome these objections to the CP formulation of a pollution hazard index for municipal leachates, the ranking equation was changed as follows:

$$R = (Q)\ (HI) \qquad \{4\}$$

where R and Q are as previously defined and
HI = the pollution hazard index for the waste.

The pollution hazard index (HI) is a toxicity index for the element within a given leachate, multiplied by a mobility index for the element in a particular leachate-clay system. The pollution hazard for the whole leachate is that for the constituent with the highest hazard within the particular leachate.

$$HI = \left(\frac{C}{DWS}\right)(100 - ATN) \qquad \{5\}$$

where C = the effective concentration of the chemical constituent,
DWS = the drinking water standard (U.S.-EPA, 1972), and
ATN = the attenuation number for the given element.

The effective concentration is defined as the concentration of the chemical constituent in the leachate plus the concentration of the constituent that may be leached from the soil or clay. When attenuation is occurring, the effective concentration is merely the concentration of the constituent in the influent leachate. When elution from the columns is occurring, as it did for the three elements B, Ca, and Mn, the effective concentration is the leachate concentration plus the concentration eluted from the column. Table 6 presents the 15 chemical constituents for which ATN values are available, ranked according to their pollution hazard, as determined by equation 5.

The results in Table 6 give a reasonable ranking of the chemical constituents in terms of what would be expected from a gross overview of the data. The ranking system has the advantage of quantifying the expected pollution hazard of a given leachate and allows comparisons of the pollution hazards of one leachate with another. The ranking system also focuses attention on the chemical constituent with the highest pollution potential. In the case of DuPage leachate, NH_4^+ was found to have the highest pollution hazard. In a fresh leachate, COD might be expected to have the highest pollution potential. However, in the DuPage leachate the hazard index clearly indicates that NH_4^+ is a pollution hazard about 30 times greater than any other constituent found in this particular leachate.

We feel that the proposed pollution hazard ranking system for municipal leachates (equation 5) overcomes the objections posed previously for the CP component of the Priority Ranking System. The toxicity index can in most cases be computed readily from a chemical analysis of the leachate.

The evaluation of the toxicity index is flexible in that drinking water standards need not be the criteria. LD_{50} values, or some other toxicity evaluation, can be used in place of drinking water standards. What we think is important is the computation of the ratio of the actual waste concentration relative to whichever toxicity evaluator is used. The mobility index, however, must be determined experimentally or estimated from the data presented in this paper. The results of this study indicate that the mobility index will be a function of the CEC of the earth material, the cations present initially on the exchange complex, the chemical composition of the leachate, and the pH of the leachate.

TABLE 6. CHEMICAL CONSTITUENTS IN DUPAGE LEACHATE, RANKED ACCORDING TO POLLUTION HAZARD

Chemical constituent	Effective concentration / D. W. standard	Toxicity index	Mobility index	Hazard index
NH_4	862/0.5	1724.	62.9	108,440.
B	(29.9 + 3.5)/1.0	33.4	111.8	3,734.
COD	1340/50	26.8	78.7	2,109.
Hg	0.87/0.002	435.	3.2	1,392.
Cl	3484/250	13.9	89.3	1,241.
Ca	(46.8 + 307.3)/250*	1.42	756.7	1,072.
Cd	1.95/0.01	195.	3.0	585.
Fe	4.2/0.3	14.0	41.6	582.
Na	748/270	2.77	84.6	234.
Mn	(0.02 + 0.02)/0.05	0.78	195.4	153.
K	501/250*	2.00	61.8	123.
Mg	233/250*	0.93	70.7	65.7
Pb	4.46/0.05	89.2	0.2	17.8
Zn	18.8/5.0	3.76	2.8	10.5
Si	14.9/250*	0.06	45.3	2.7

*Actual value not established by EPA; therefore it was assumed to be the same as chloride.

SECTION 6

CONFIRMATION OF LABORATORY COLUMN STUDIES BY COMPARISON WITH FIELD DATA[1]

ABSTRACT

The results of the laboratory column leaching experiments were checked at the DuPage County sanitary landfill and at other existing landfills where detailed field data are available. These field data clearly show a "hardness halo" corresponding to the Ca release observed in the column experiments. The relative attenuation rates of some of the ions are also confirmed by the field data.

Laboratory results show that the leachate reduced the hydraulic conductivity of the columns during the experiment. Although similar change in field hydraulic conductivity was not clearly demonstrated, the field data suggest that it took place.

These results suggest that overall pollution from landfill leachate would be reduced by designing earth material landfill liners for higher permeability. Properly designed liners would selectively attenuate the toxic pollutants from the leachate and allow the ground water to dilute the nontoxic components which can be tolerated at much higher concentrations without harmful effects. The study raises some basic questions on monitoring systems and landfill design which should be addressed by regulatory agencies responsible for environmental quality.

INTRODUCTION

This paper principally relates two phenomena noted in the laboratory to field observations around sanitary landfills: the elution of large amounts of the calcium ion from the study columns (Fig. 3) and the reductions in hydraulic conductivities which resulted from the introduction of leachate to the clay-sand mixtures. It is felt that the testing of laboratory results in field situations is necessary before the data may be used in sanitary landfill design.

RESULTS AND DISCUSSION

Hardness Halo

Figure 3 (Section 5) illustrates the negative attenuation or elution of

[1] Authors: K. Cartwright, R. A. Griffin, and R. H. Gilkeson.

Ca, Fe, and Mn from the columns containing 2, 8, and 16% montmorillonite clay in sand. The relative concentrations greater than 1 indicate that Ca and to a lesser extent Fe and Mn are eluting from the column at much greater concentration than the influent leachate at various pore fractions. The area under the Ca curves can be seen to increase in proportion to the percentage of clay in the column, was quantified in Section 5 by integrating between pore fraction 1 and 11, and was assigned a relative attenuation number (ATN) as shown in Table 4 (Section 5).

The elution of Ca from the columns was attributed to an ion-exchange mechanism; the replacing of the Ca bonded to the clays at their cation exchange positions by other ions in the leachate.

Soils in much of Illinois are carbonate rich, with the clays generally having Ca in the cation exchange position, and have free carbonates in all except the leached zone of the soils. The presence of excessive hardness in the vicinity of sources of pollution has appeared in a number of articles, but is rarely discussed as to its origin. An example is found in a DuPage County study (Fig. 7, from Zeizel et al., 1962). There are two areas of the county where the hardness, as $CaCO_3$, in the shallow carbonate aquifer exceeds 1000 parts per million (ppm). The eastern area is a fairly heavily developed residential area and the glacial drift, which protects the aquifer from pollution, is relatively thin. No specific source of the high hardness can be established; however, it is most likely due to a high concentration of home septic systems. The western area of high hardness near West Chicago is thought to have resulted from the discharge of large volumes of waste chemical salts to surface ponds.

Other examples can be found in Anderson and Dornbush's (1967) study of a sanitary landfill in South Dakota, and Walker's (1969) discussion of groundwater pollution in Illinois. Most recently, Henning et al. (1975) showed high calcium in monitoring wells very close to a landfill trench at Mentor, Ohio; the Ca concentrations both decreased with distance from the fill and were lower in the refuse than in the closest wells.

Hughes et al. (1971) published the results of studies of five landfills in northeastern Illinois, including the Old DuPage County landfill from which the leachate was taken for this study. Monitoring continued for three years following the completion of that report. Figure 8 was drawn, using data from the Winnetka and Old DuPage landfills.

The Winnetka data (top, Fig. 8) shows considerable scatter. This may be partly due to a mixture of points, some in the fine-grained alluvium and some in the glacial till which have somewhat different properties. However, these data suggest that the hardness approaches background within 9 to 15 meters of the refuse which is somewhat less than the distance that the chloride ion travelled (Hughes et al., 1971). Note that the four data points from piezometer nest LW3 follow this pattern.

The till under the Old DuPage landfill clearly illustrates the increase, then decrease in hardness. The till is separated from the refuse by 1 to 1.5 meters of sand. The hardness returns to background within about 1.5 meters of

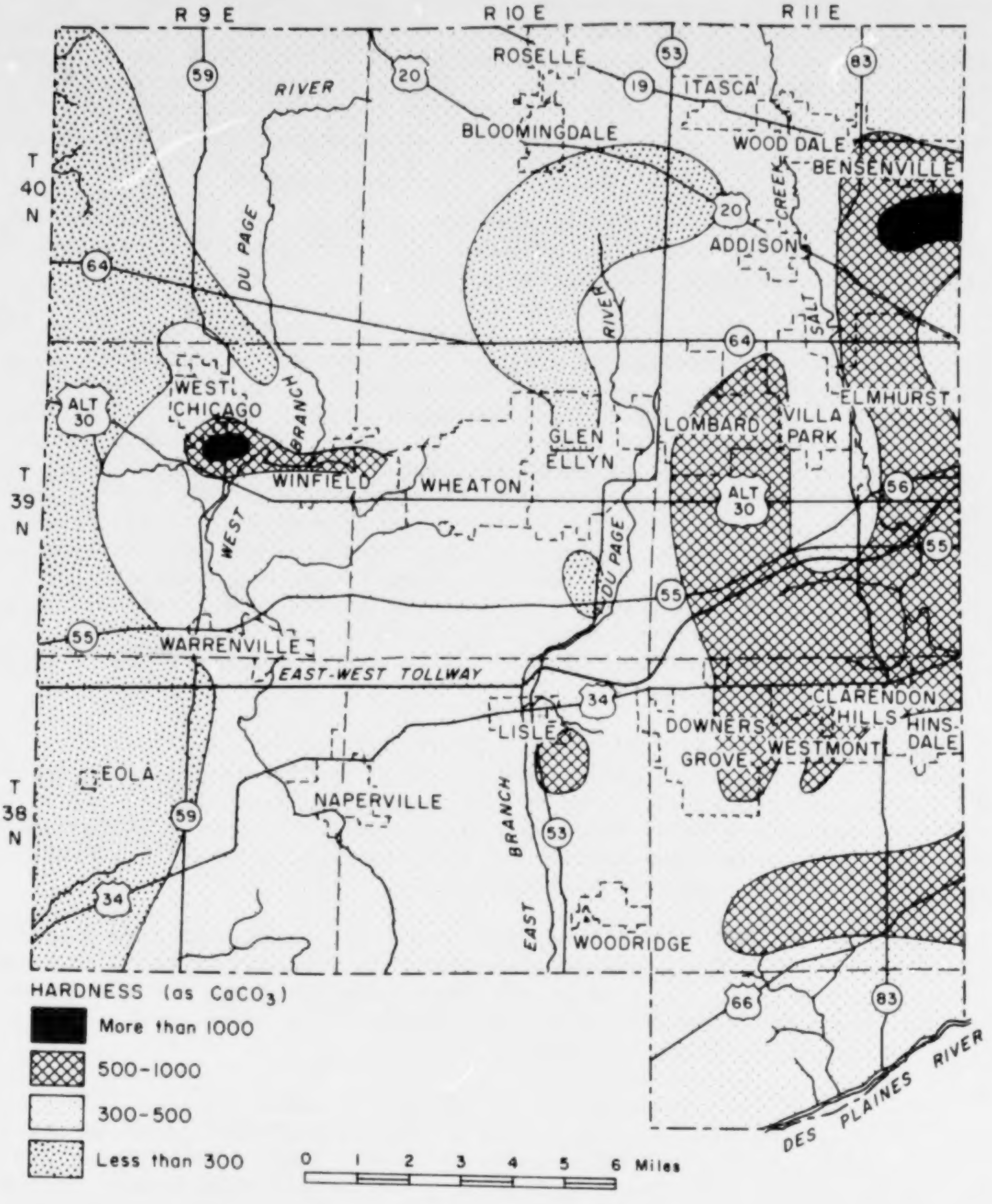
R 9 E
R 10 E
R 11 E
T 40 N
T 39 N
T 38 N
ROSELLE
ITASCA
BLOOMINGDALE
WOOD DALE
BENSENVILLE
ADDISON
SALT CREEK
DU PAGE RIVER
WEST BRANCH
WEST CHICAGO
WINFIELD
WHEATON
GLEN ELLYN
LOMBARD
VILLA PARK
ELMHURST
WARRENVILLE
EAST-WEST TOLLWAY
LISLE
DOWNERS GROVE
WESTMONT
CLARENDON HILLS
HINSDALE
EOLA
NAPERVILLE
EAST BRANCH
WOODRIDGE
DES PLAINES RIVER
59
20
53
19
83
64
ALT 30
56
55
34
66
HARDNESS (as $CaCO_3$)
More than 1000
500-1000
300-500
Less than 300
0 1 2 3 4 5 6 Miles

Figure 7. Hardness of water, expressed as $CaCO_3$, in the Silurian Dolomite aquifer in DuPage County, northeastern Illinois (from Zeizel et al., 1962).

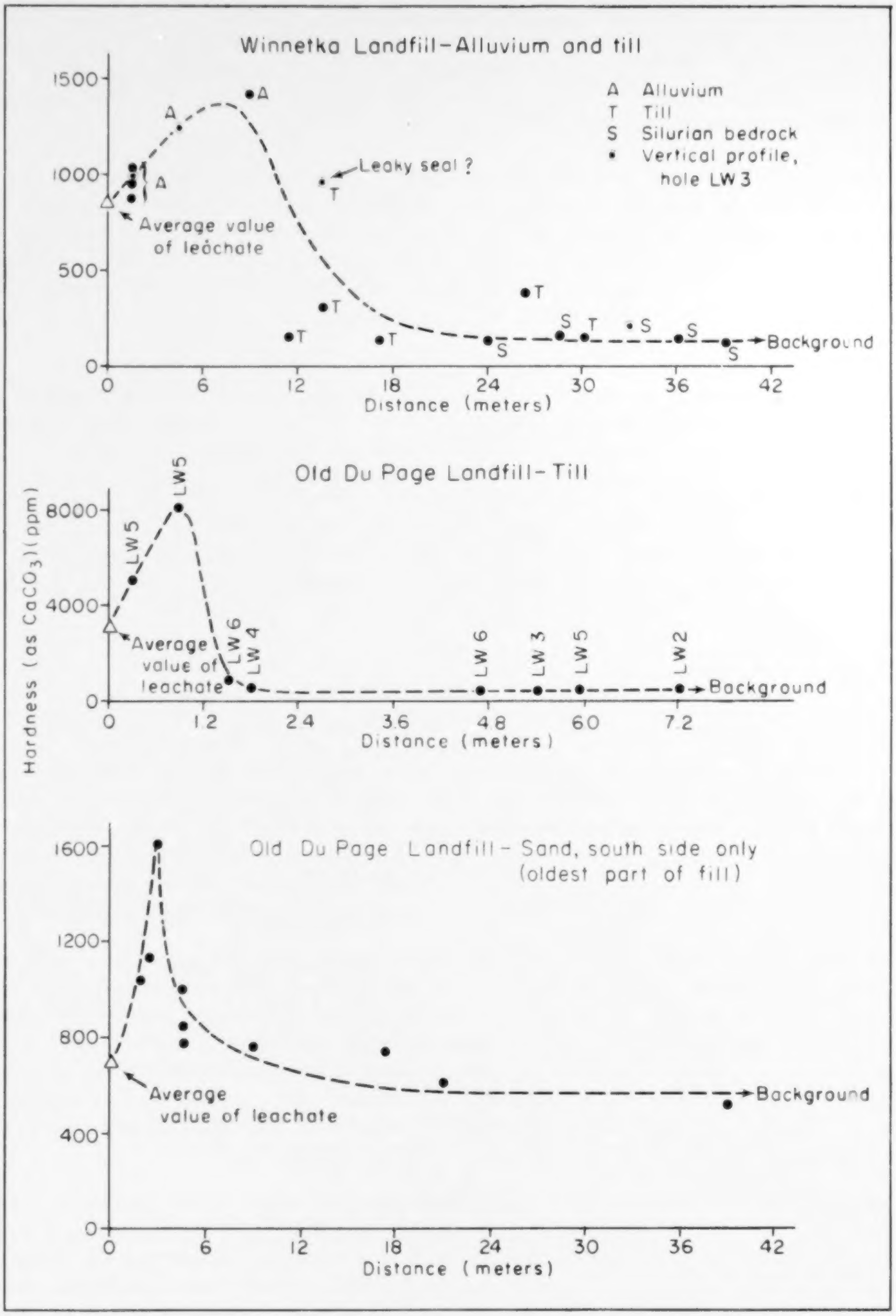

Figure 8. "Hardness halo" effect shown as a function of distance (m) from the Winnetka and DuPage landfills in northeastern Illinois.

travel, about half the distance of the estimated travel of the chloride ion (Hughes et al., 1971). Note, in particular, the values shown for piezometer nests LW5 and LW6. These data points are all for the younger, northern part of the fill; data from the older parts of the fill do not fit the same curve (all hardness concentrations fall too low).

The surficial sand transmits leachate-contaminated water south from the older parts of the DuPage landfill and shows a similar hardness distribution. The hardness levels are much lower in the old refuse in this area, and all the values reflect that lower concentration. The hardness returns to background levels within 9 to 15 meters; however, chloride ion has moved 240 to 300 meters in the permeable sand layer.

All these data clearly show the presence of the "hardness halo" resulting from the movement of leachate into the surrounding till and sands, and that the rate of the hardness front is less than that of the chloride ion. The chloride ion is probably the best tracer of this type of pollution in this environment. The distance of travel varied from slightly less to approximately 10% of that of the chloride ion; this probably is controlled by the nature of the materials, cation exchange reactions, concentrations in the leachate, and ground-water flow rates. Nevertheless, all the data show an increase in the hardness of the water in the sediments over that in the leachate.

Hydraulic Conductivity

The results of initial hydraulic conductivity and bulk density measurements of the column contents in the laboratory study are presented in Table 3. These data indicate that a wide range of hydraulic conductivities, with values in agreement with those expected under field conditions from similar materials (Todd, 1959) were observed. The relatively high bulk densities and slow flow rates used in this study closely simulate the conditions observed in the field. This lends credence to the extrapolation of the results and conclusions of the laboratory studies to those obtained in the field.

During the initial stage of the experiment, the columns were leached with deionized water until steady state conditions were achieved. The columns containing low percentages of clay reached hydraulic equilibrium relatively rapidly while the high percentage clay columns required leaching for well over a month to achieve steady manometer readings. When hydraulic equilibrium was achieved, as indicated by steady flow rates and relatively constant manometer readings from the five manometers located over the entire length of each column, the leachate was added to the columns.

Significant reductions in hydraulic conductivity and significant differences in the reductions between natural and sterile leachate were observed. The results of hydraulic conductivity changes observed in columns containing montmorillonite, kaolinite and illite clays are presented in Figures 9, 10, and 11. The data presented in these figures were statistically smoothed using the five-member moving-average method to show more clearly the trends in the data. The raw data were statistically analyzed to determine whether significant differences in hydraulic conductivity occurred between

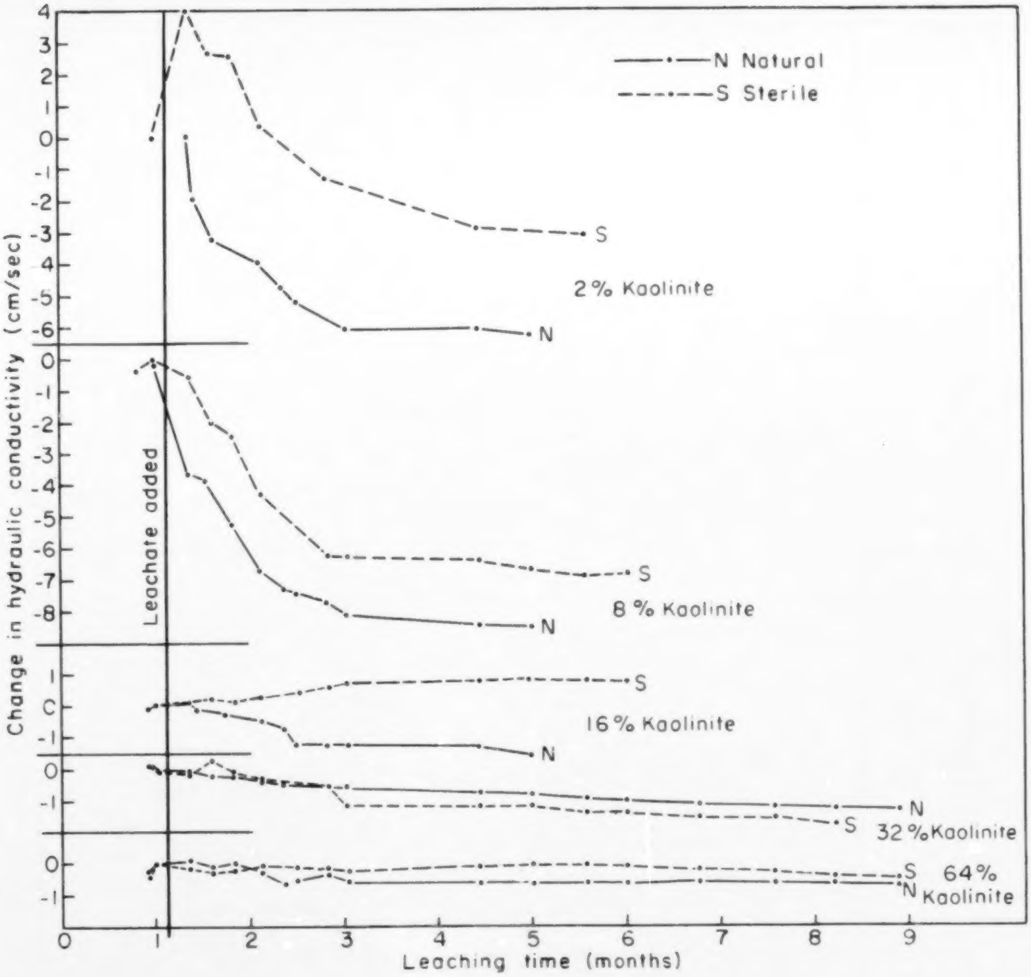

Figure 9. Hydraulic conductivity of kaolinite-sand columns as a function of leaching time.

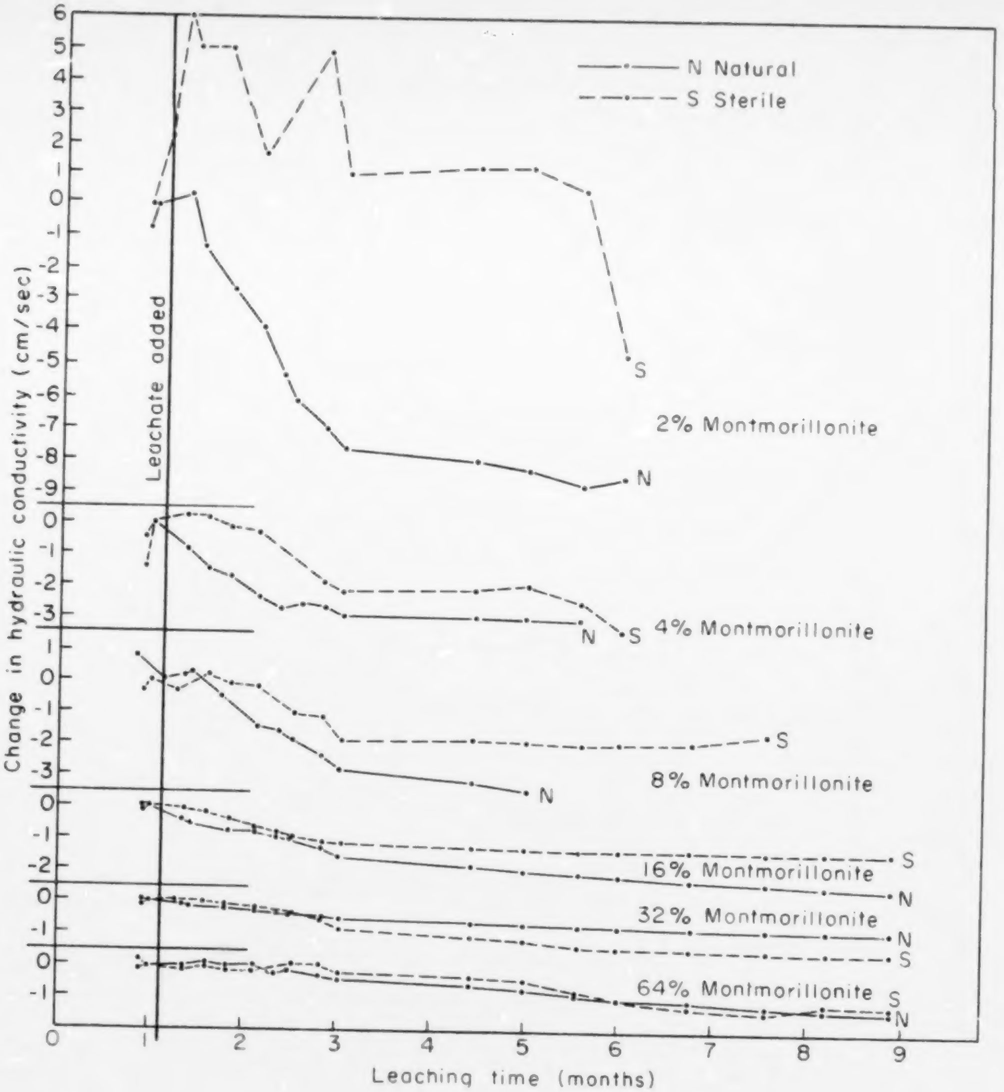

Figure 10. Hydraulic conductivity of montmorillonite-sand columns as a function of leaching time.

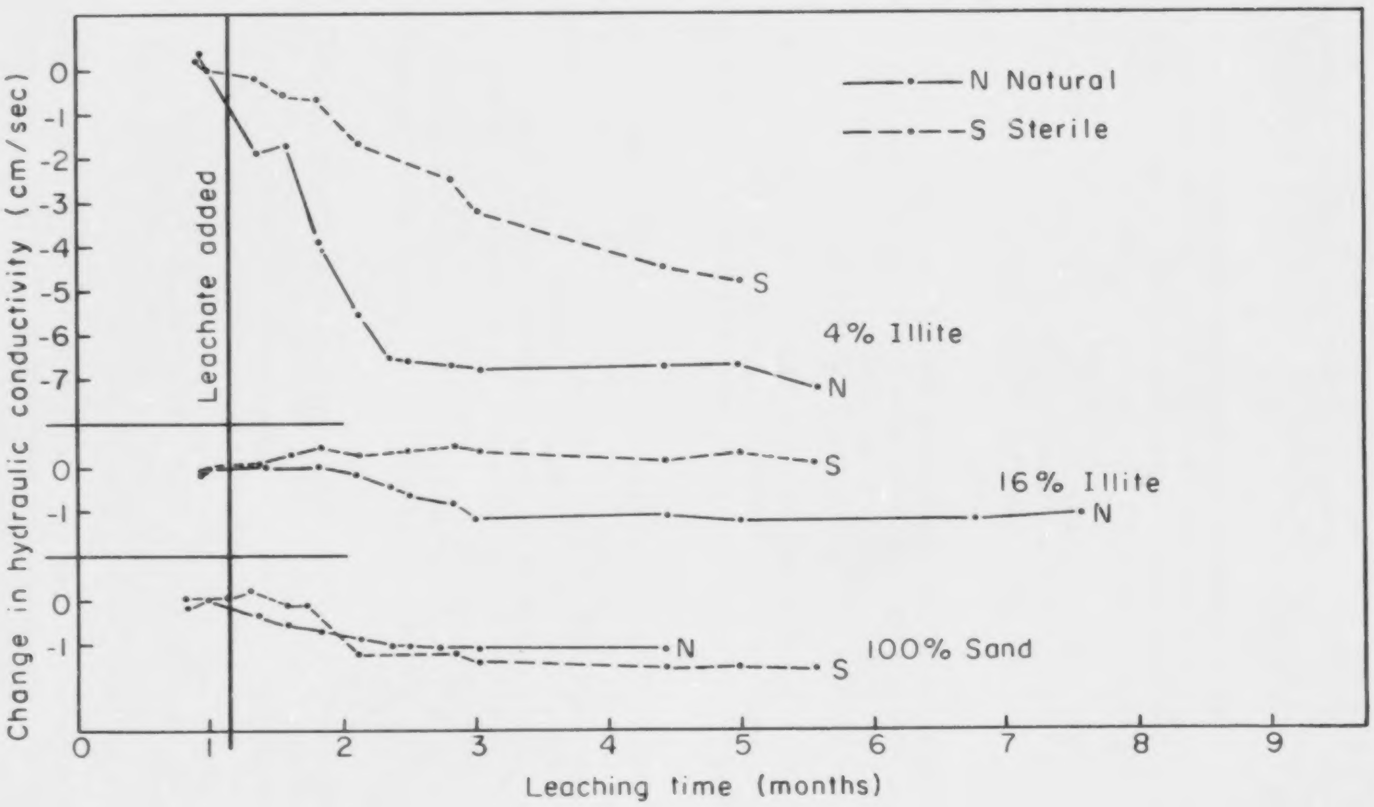

Figure 11. Hydraulic conductivity of illite-sand columns as a function of leaching time.

sterile and natural leachate. The data from the columns containing 4% kaolinite were rejected from the analysis when they were found to deviate by more than 3 standard deviations from the overall mean change in hydraulic conductivity observed for all other columns. The manometer readings indicated that the outflow tubes were plugged. The reason why only 4% kaolinite treatments had this problem is not clear.

The results of the statistical analysis indicated that columns leached with natural leachate had significantly (.05 level) greater reductions in hydraulic conductivity than those leached with sterile leachate. This result is illustrated clearly in Figures 9, 10, and 11. Furthermore, the statistical analysis showed that columns containing montmorillonite had significantly greater average reductions in permeability than kaolinite or illite and that there was no significant difference between kaolinite and illite. This result is consistent with the swelling nature of montmorillonite clay and is not surprising.

Field data to support this conclusion are not as clear as for the "hardness halo." Fewer field tests have been made for hydraulic conductivities than chemical tests for water quality. In addition, field tests may be accurate only to approximately a half-order of magnitude.

At the Winnetka landfill (Hughes et al., 1971), 23 hydraulic conductivity tests were conducted, 7 on refuse, 4 on alluvium, and 7 on till. These data are too scattered to show any significant differences with distance from the refuse.

At the Old DuPage County landfill, 34 field hydraulic conductivity tests were made, 14 on refuse, 14 on sand, and 6 on till. The data on the hydraulic conductivity of the sand (all south of the fill) suggest some reduction in hydraulic conductivity. The 10 tests made on monitoring wells less than 6 meters from the fill have a mean hydraulic conductivity of 4.32×10^{-4} cm/sec (range 1.9×10^{-3} to 1.9×10^{-7}), and those monitoring wells greater than 12 meters from the refuse (4 tests) have a mean conductivity of 2.59×10^{-3} cm/sec (range 7.6×10^{-3} to 9.5×10^{-4}). The data are not statistically significant, but they do suggest a hydraulic conductivity reduction similar to that noted in the laboratory.

The reductions in hydraulic conductivity observed in the laboratory study with the DuPage leachate seem particularly significant. This is due to the fact that the DuPage leachate is approximately 15 years old (Hughes et al., 1971) and contains a relatively low percentage of organic compounds which are readily degradable by microorganisms (Table 2). In addition, this leachate has a low nutrient status with both phosphate and sulfate being absent in detectable quantities. Much higher amounts of microbial growth and plugging might be expected from a younger leachate.

The results have led to the conclusion that if clay liners, natural or man-made, of similar composition to those used in this study are used in municipal landfills, significant reductions in hydraulic conductivity can be expected due to microbial growth. Further, slightly higher reductions in hydraulic conductivity can be expected from montmorillonite clays, apparently due to their swelling tendency. It was also concluded that Mn and/or Fe may be leached from clay surfaces in substantial amounts under highly anaerobic conditions but may not be leached under mildly anaerobic conditions.

SECTION 7

EFFECT OF pH ON EXCHANGE-ADSORPTION OR PRECIPITATION OF LEAD FROM MUNICIPAL LEACHATES BY CLAY MINERALS[1]

ABSTRACT

The capacity of kaolinite and montmorillonite clay minerals to remove Pb from municipal landfill leachates and the mechanisms by which removal is achieved were studied to evaluate the potential usefulness of clay minerals as liners for waste disposal sites under conditions of varying pH and ionic competition.

Montmorillonite was found to remove as much as 5 times more Pb from various solutions than did kaolinite. Results indicated that Pb removal was reduced as much as 85% by leachate when compared to the amounts removed from pure $Pb(NO_3)_2$ solutions. A precipitate was found to form in leachates at pH values above 5 and was identified as $PbCO_3$. The complexing capacity of DuPage leachate for Pb was measured and the extent of complexation was found to be 11%. The higher-ionic-strength Blackwell leachate had no measurable complexing capacity for Pb. Increased adsorption of $Pb(NO_3)_2$ was found to correspond to the appearance of Pb-hydroxyl species in solution.

It was concluded that Pb removal from solution is primarily a cation exchange-adsorption reaction that is affected by pH and ionic competition. It was also concluded that formation of Pb-organic complexes are of secondary importance in landfill leachates due to competition from high concentrations of other cations. At pH values above 6, a large increase in Pb removal from solution by clay can be expected, due to either increased adsorption of Pb-hydroxyl complexes or formation of $PbCO_3$ in landfill leachates.

The thickness of clay liners necessary to remove Pb from solutions of $Pb(NO_3)$, 0.1 M NaCl, and landfill leachates at concentrations ranging between 10 and 1000 ppm Pb and at pH values from 3 to 8 were computed. Some undesirable environmental consequences of the reversible Pb exchange-adsorption reaction with clay may ensue where pH and ionic competition are unfavorable.

INTRODUCTION

This section reports the results of an investigation, the purpose of which was to determine the capacity of the two major clay mineral types for removing Pb from solution and the effect municipal leachates have on this capacity at various pH values. Another purpose of the investigation was to gain insight into the mechanisms responsible for attenuation of Pb as well as to evaluate the potential use of clay minerals as liners for waste disposal sites.

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[1] Authors: R. A. Griffin and N. F. Shimp.

Lead was chosen for study because documented evidence shows that low Pb levels in drinking water can cause death to humans. In one case in Australia, 94 adults died of chronic lead poisoning because throughout childhood they drank water collected from roofs of houses painted with lead-pigmented paint (Henderson, 1955). There is also evidence (Broadbent and Ott, 1957) that organic chelates form with hydrolyzable metals and that they may make Pb more mobile in soils or clay liners when municipal leachates are present than in effluents that do not contain high concentrations of organic compounds.

EXPERIMENTAL

The Pb removal studies were conducted by placing a known weight of clay, between 0.100 and 1.000 g, into a 125 ml Erlenmeyer flask. The weight of clay used was chosen to give an estimated 20 to 50% change in the Pb concentration of the solution at equilibrium. A 50 ml aliquot of either deionized water, 0.1 M NaCl solution, or leachate and then a 2 ml aliquot of a $Pb(NO_3)_2$ solution were pipetted into the flask. The pH of the solutions were adjusted with either HNO_3 or NaOH over the pH range of interest, and the volumes of acid or base added were recorded. The volumes added were usually less than 1 ml. The flasks were tightly stoppered, and as a result the CO_2 liberated from the leachate solutions caused a slight positive pressure in the flask, which aided in maintaining anaerobic conditions during equilibration. (For a period of time after addition of acid, the stoppers were removed to relieve excessive pressure, and then the flasks were restoppered.) The results of rate studies indicated that 4 hours were necessary for Pb in leachate to equilibrate with kaolinite. This result is in agreement with Beevers (1966), who found that $Pb(NO_3)_2$ solutions equilibrated in from 1 to 12 hours, depending on the clay mineral. The samples in this study were shaken for at least 24 hours in a constant temperature bath at 25 ± 0.5^{o} C to insure equilibration. The equilibrium pH was recorded, the samples were centrifuged, and the solutions were analyzed for their Pb concentration by atomic absorption. The difference between the initial concentration and the equilibrium concentration was used to compute the amount of Pb removed from the solution at the particular pH by a given clay mineral. This procedure was carried out for a range of initial Pb concentrations that varied between 10 and 1,000 ppm.

The resulting data were plotted as amount of Pb removed from solution per gram of clay versus pH. The resulting family of curves allowed construction of adsorption isotherms for any individual pH value of interest throughout the pH range 3 to 6. Representative adsorption isotherms and plots of the data according to the Langmuir (1918) adsorption equation were constructed at various pH values to determine the maximum amount of Pb that could be adsorbed from the various solutions by the two clay minerals and to try to gain insight into the mechanisms of adsorption. The Langmuir (1918) equation in its linear form is:

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \qquad \{6\}$$

where C is the equilibrium concentration of Pb, x/m is the amount of Pb adsorbed per unit mass of clay, 1/b is the slope where b is the adsorption maximum for Pb, and k equals the slope/intercept where k is a term relating to the energy of adsorption.

The ability of the two municipal leachates to complex metal ions, in particular Pb, was studied. The leachates were centrifuged at 1000 rpm for 10 minutes and then filtered through a 0.45 µm pore-size Millipore membrane held in an anaerobic bacteria filter holder under argon pressure. The leachate obtained after centrifugation and filtration was considered to contain only soluble organics and was used in the complexation studies. Successive aliquots of Pb were added to the leachate and equilibrated for several hours. The concentration of free and complexed lead ions in solutions were determined from pulse polarographic wave heights using the methods and equipment described by Gadde and Laitinen (1973a).

Lead was removed from leachate solutions as a white precipitate at pH values greater than 6. The precipitate was separated from solution on a 0.45 µm Millipore membrane, washed with deionized water and dried at room temperature. The chemical compound was then identified from its X-ray diffraction pattern.

RESULTS

The results of Pb removal from 25° C solutions of DuPage leachate by kaolinite and montmorillonite clay minerals were plotted as a function of pH in Figures 12 and 13, respectively. Similar results obtained for Pb removal from Blackwell leachate by kaolinite are shown in Figure 14.

The data presented indicate that Pb removal from landfill leachate increases with increasing pH values and with increasing concentration of Pb in solution. Increasing Pb concentration is indicated on the figures by increasing alphabetical order, and the initial Pb concentration, weight of clay used, micrograms of Pb added, and volume of solution that correspond to the alphabetical designations are given in Table 7. A blank (no clay) solution of leachate with Pb added was carried along through the experiment and the results of these also appear on the figures.

Data for Pb removal from leachate plotted as a family of curves of increasing concentration have the advantage that sorption isotherms may be constructed from the plot, by using the information given in Table 7, for any desired pH value from pH 3 to pH 6.

Pb sorption isotherms can be constructed from these plots by first placing a vertical line across the family of curves at the pH of interest. The amount of Pb removed from solution is found on the graph at the points where the vertical pH line intersects each curve. The equilibrium Pb concentrations that correspond to the chosen pH value are then computed from the amounts of Pb removed at each concentration, as determined from the graph and the information for each Pb curve given in Table 7 by using the following relation:

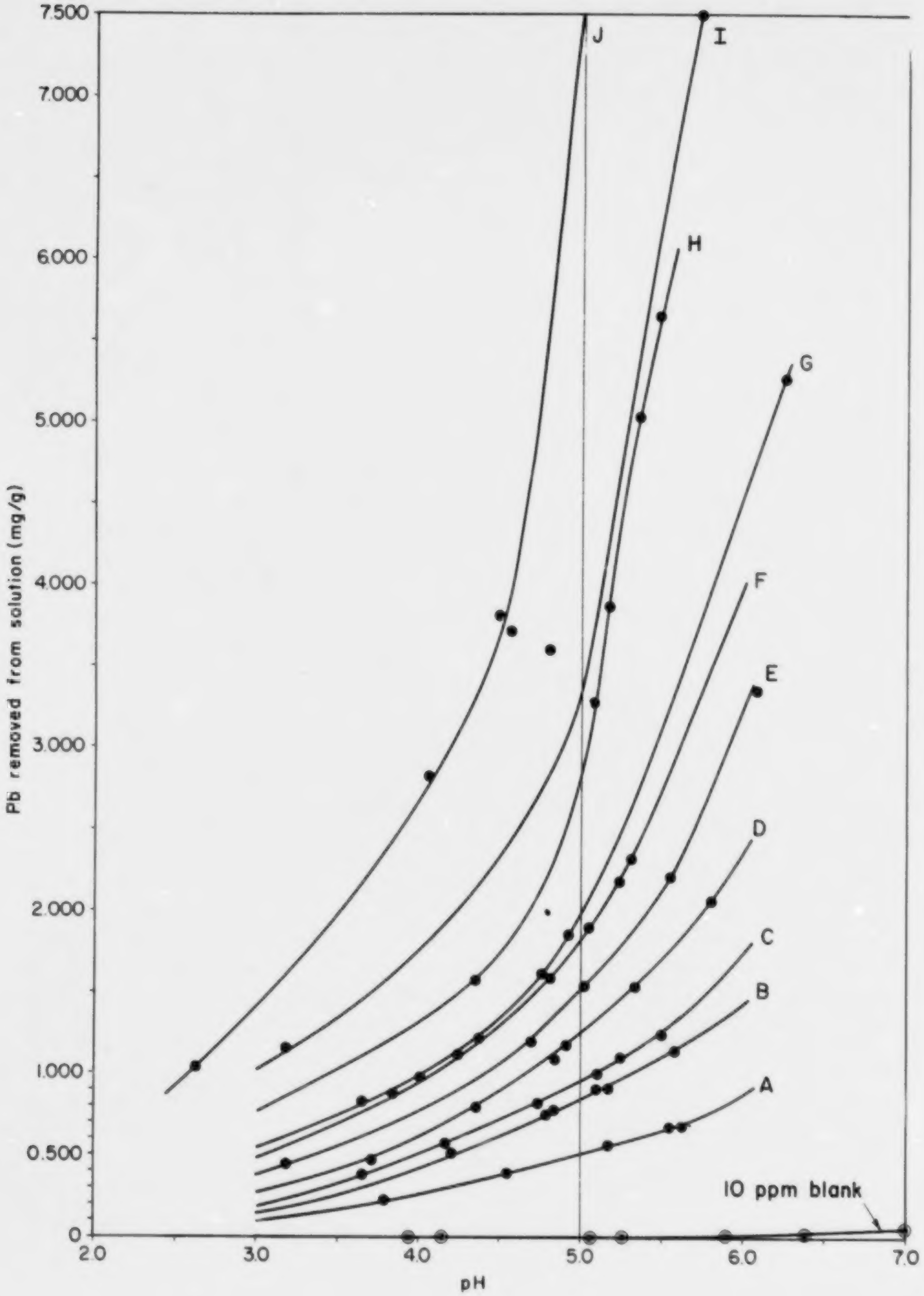

Figure 12. The amount of Pb removed from DuPage leachate by kaolinite at 25° C plotted as a function of pH.

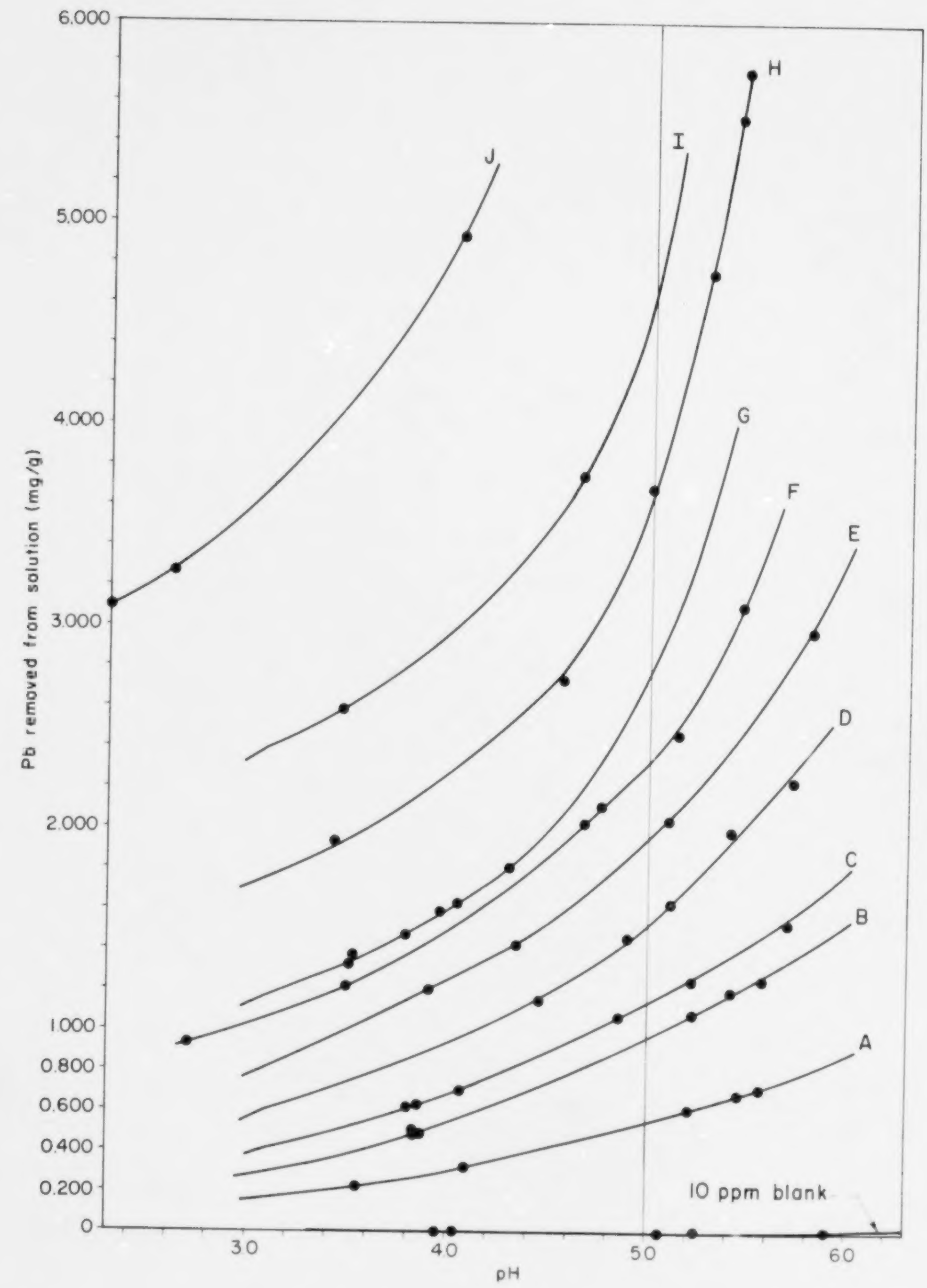

Figure 13. The amount of Pb removed from DuPage leachate by montmorillonite at 25° C plotted as a function of pH.

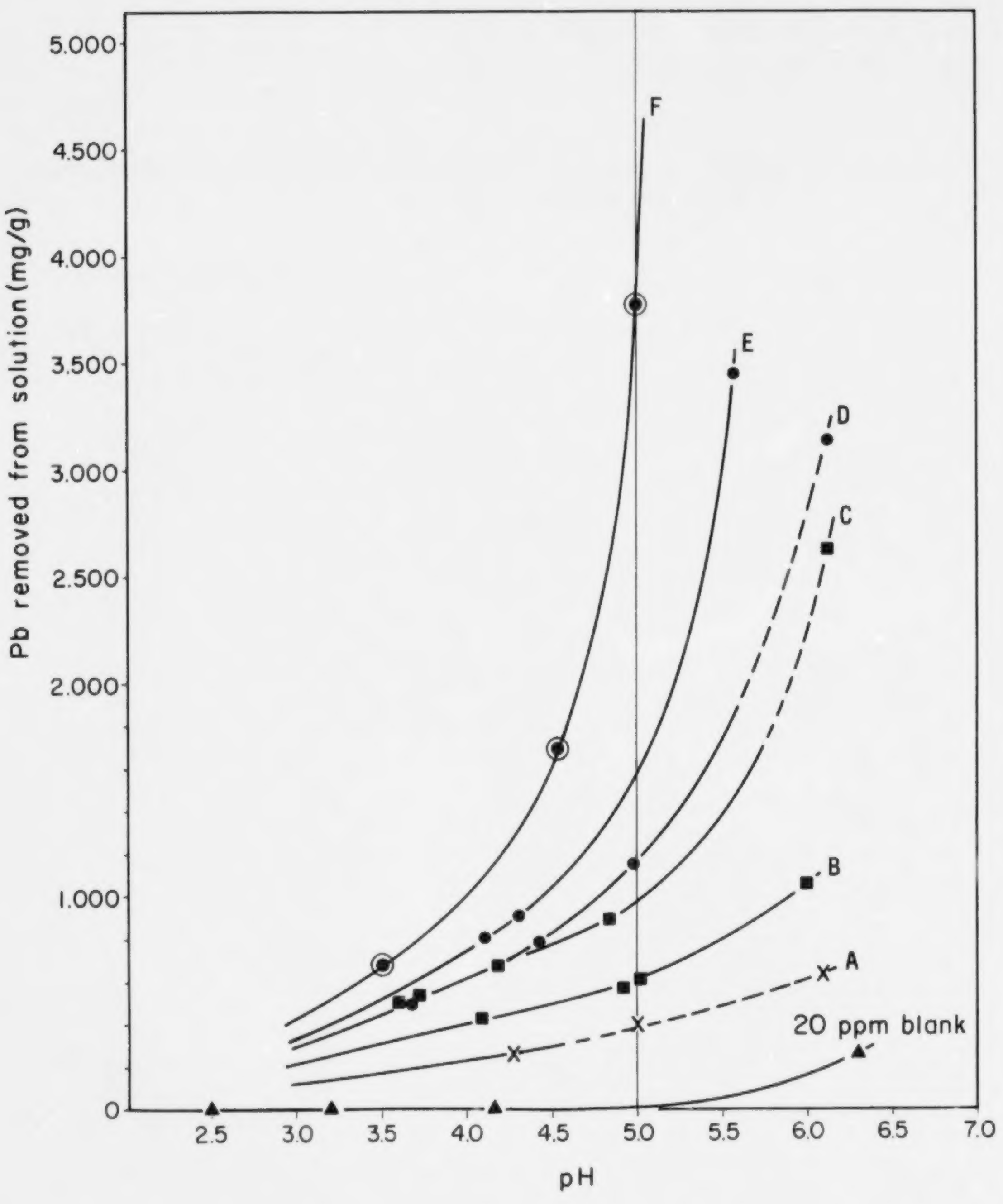

Figure 14. The amount of Pb removed from Blackwell leachate by kaolinite at 25° C plotted as a function of pH.

TABLE 7. Pb REMOVAL PARAMETERS USED TO COMPUTE SORPTION ISOTHERMS FROM 52 ml REACTION VOLUMES

	Curve	Initial Pb concentration (ppm)	Pb added (micrograms)	Clay weight (grams)
DuPage leachate - kaolinite (Fig. 2)	A	9.62	500	0.500
	B	19.23	1,000	0.500
	C	38.46	2,000	1.000
	D	57.69	3,000	1.000
	E	76.92	4,000	1.000
	F	96.15	5,000	1.000
	G	115.38	6,000	1.000
	H	153.85	8,000	1.000
	I	192.31	10,000	1.000
	J	384.62	20,000	1.000
DuPage leachate - montmorillonite	A	9.62	500	0.500
	B	19.23	1,000	0.500
	C	38.46	2,000	1.000
	D	57.69	3,000	1.000
	E	76.92	4,000	1.000
	F	96.15	5,000	1.000
	G	115.38	6,000	1.000
	H	153.85	8,000	1.000
	I	192.31	10,000	1.000
	J	384.62	20,000	1.000
Blackwell leachate - kaolinite (Fig. 4)	A	19.23	1,000	1.000
	B	38.46	2,000	1.000
	C	76.92	4,000	1.000
	D	96.15	5,000	1.000
	E	192.31	10,000	1.000
	F	288.46	15,000	1.000

$$\text{Equil. Pb} = \frac{\text{Pb added } (\mu g) - (\text{Pb removed } (\mu/g) \times \text{wt. clay}}{\text{sample volume}}$$

Pb sorption curves were constructed by this method for several pH values from the plots given in Figures 12, 13, and 14. Representative curves are presented in Figure 15 along with sorption isotherms obtained at pH 5.0 and 25° C for Pb sorption from $Pb(NO_3)_2$ solutions and 0.1 M NaCl solutions, followed by the DuPage and Blackwell leachates, respectively.

The sorption curves for the two leachates show a sharp upswing occurring at equilibrium concentrations of approximately 200 ppm Pb. Qualitatively identical curves, also with a sharp upswing at about 200 ppm Pb, were obtained by using montmorillonite clay. The data presented in Figure 13 may be used to verify this finding. Sorption isotherms computed from Figures 12, 13, and 14 at pH 3.0 or 4.0 did not exhibit the sharp upswing. A sharp upswing in a sorption isotherm at higher concentrations is generally viewed as initiation of precipitation of an insoluble compound. The fact that the sharp rise in Pb removal occurred at about 200 ppm Pb under the CO_2 partial pressures in the flasks, while at pH 4.0 no sharp increase was observed, is consistent with solubility computation which assume a mechanism of $PbCO_3$ formation.

To predict the maximum amounts of Pb that could be sorbed by the two clays from the various solutions, the kaolinite sorption data plotted in Figure 15 and the sorption data obtained for montmorillonite were plotted according to the Langmuir adsorption isotherm equation. The results are illustrated in Figure 16.

The Langmuir equation was found to describe the data obtained for $Pb(NO_3)_2$ sorption by both kaolinite and montmorillonite and for Pb sorption from 0.1 M NaCl solutions by kaolinite over the entire concentration range studied. The results obtained for the leachates, however, were somewhat different. The Langmuir equation was found to describe the sorption up to concentrations between 30 and 40 ppm, at which point a sharp change in slope occurred, giving two distinct linear regions to the isotherms. The adsorption maximums computed from the slopes of the lines shown in Figure 16 are given in Table 8. From the values in Table 8 a quantitative estimate of the sorption differences noted in Figure 15 and a comparison of the sorption capacities of the two clays can be made. In $Pb(NO_3)_2$ solution, montmorillonite sorbed approximately five times more Pb than kaolinite, while in DuPage leachate it sorbed less than twice as much as kaolinite. This result indicates that the competitive ions contained in landfill leachate affect the relative sorption affinity of Pb for the montmorillonite; i.e., leachate reduced Pb sorption by montmorillonite proportionately more than it reduced Pb sorption by kaolinite.

DISCUSSION

The data presented above suggest that several mechanisms are responsible for removal of Pb from solutions of varying ionic composition and pH.

Precipitation was found to be an important mechanism in landfill leachates, as is shown by the removal of Pb from the blank solutions, which con-

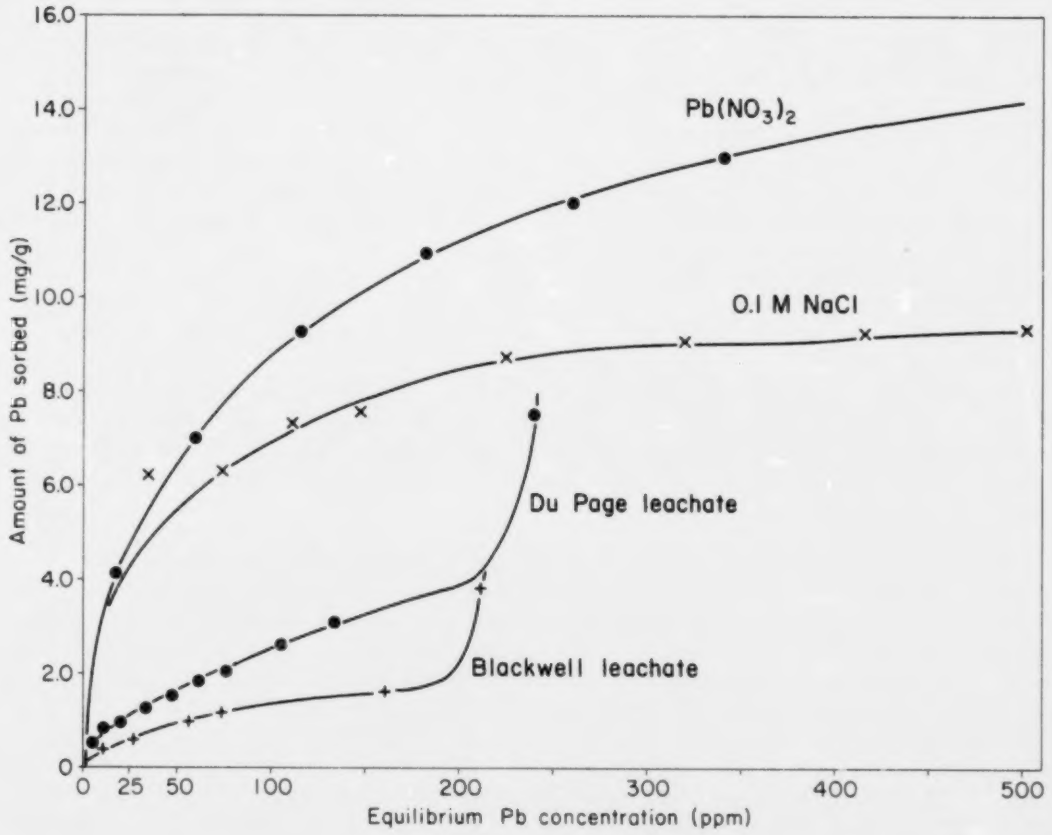

Figure 15. The amount of Pb sorbed per gram of kaolinite at pH 5.0 and 25° C plotted as a function of the equilibrium Pb concentration.

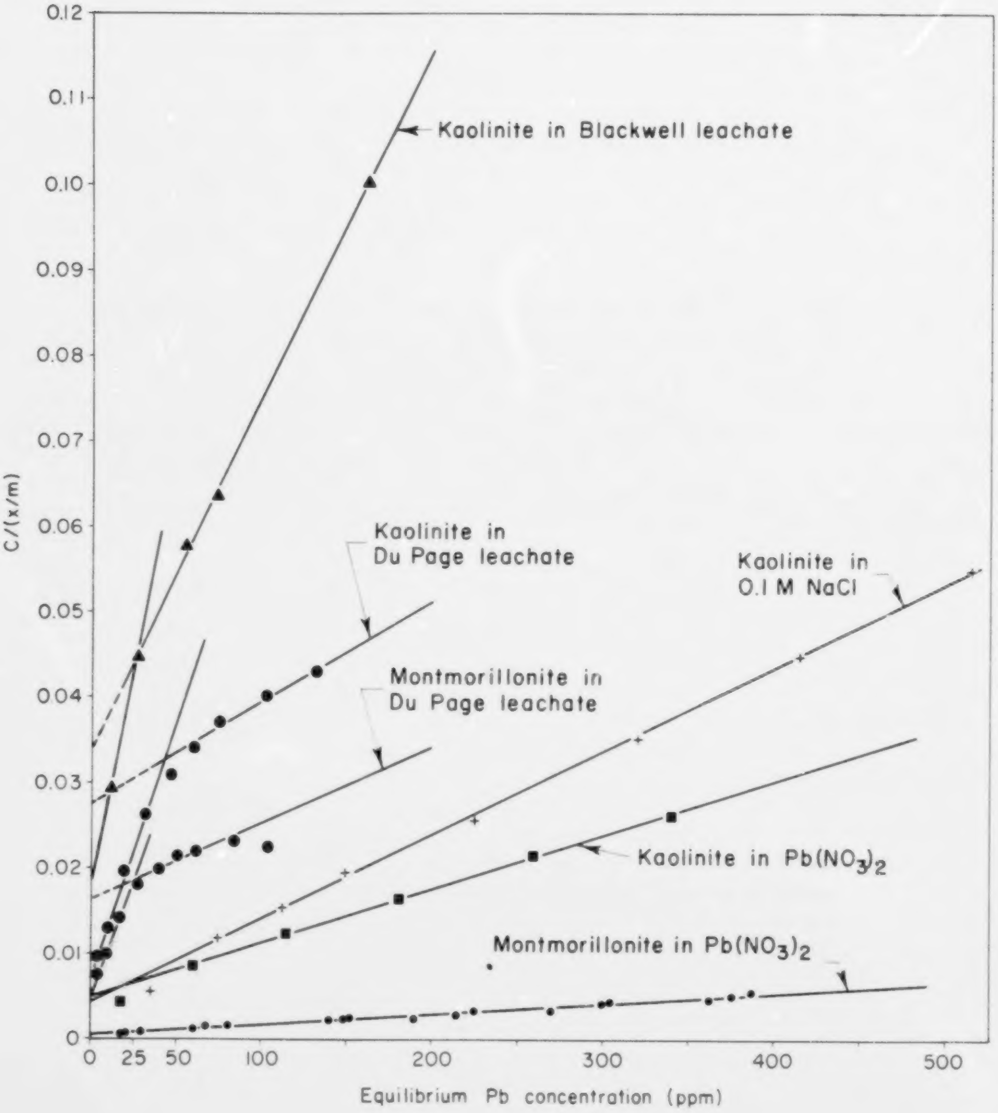

Figure 16. Pb sorption data for kaolinite and montmorillonite at pH 5.0 and 25° C plotted according to the Langmuir isotherm equation.

TABLE 8. MAXIMUM REMOVAL OF Pb FROM pH 5.0 and 25° C SOLUTIONS COMPUTED USING THE LANGMUIR EQUATION

	Micrograms/g		Meq Pb^{++}/100 g clay	
	Region 1	Region 2	Region 1	Region 2
KAOLINITE				
$Pb(NO_3)_2$	--	15,914	--	15.36
0.1 M NaCl	--	10,240	--	9.88
DuPage leachate	1,680	8,530	1.62	8.23
Blackwell leachate	986	2,401	0.95	2.32
MONTMORILLONITE				
$Pb(NO_3)_2$	--	82,428	--	79.56
DuPage leachate	1,811	11,133	1.75	10.75

tained no clay (Figures 12, 13, and 14). Losses of Pb from the DuPage leachate were observed at pH values greater than about 6 and in Blackwell leachate at pH values above 5. A white precipitate was observed forming in the leachate solutions at pH values greater than 6. It was filtered out, and the chemical compound was identified by its X-ray diffraction pattern as a highly crystalline $PbCO_3$. The peaks were sharply defined, and no peaks other than those attributed to $PbCO_3$ were observed. This is offered as evidence that $PbCO_3$ formation was the compound responsible for Pb removal from leachate solutions at the higher pH values, and it is presumed to be the cause of the apparent formation of a precipitate at concentrations of Pb greater than 200 ppm observed in the sorption isotherms (Figure 15).

Stumm and Morgan (1962) showed that the occurrence of metal hydroxyl species can affect the sorption of hydrolizable metal ions. They found that the pH at which metal hydroxyl species formed corresponded to the pH at which metal ion sorption became significant. To check the role of hydrolysis of the Pb ion on its sorption by clay at various pH values and in solutions where precipitate formation did not effect Pb removal, the distribution of various hydroxyl species in a 4×10^{-4} M $Pb(NO_3)_2$ solution in the pH range 3 to 8 was obtained from Gadde and Laitinen (1973b), who computed the species distribution by using the constants given by Olin (1960). The distribution of Pb hydroxyl species, along with data obtained for sorption by kaolinite from a solution with an initial concentration of 4×10^{-4} M Pb as $Pb(NO_3)_2$, is illustrated in Figure 17.

It is evident from the plots in Figure 17 that species other than Pb^{++} are relatively insignificant (<1%) at pH values less than 6. Sorption at pH values below 6 are not related to the hydroxyl species of Pb, but rather to Pb^{++} ion. The decrease in Pb sorption at low pH values is apparently due to an increase in competition for sorption sites, with H^+ and its related competitive effects on Pb sorption caused by the dissolution of Al^{+++} ions from the clay crystal lattice (Grim, 1968). At pH values above 6, a sharp rise in Pb sorption occurred coincident with the formation of hydroxyl Pb species. It therefore seems likely that at least a portion of the observed increase in Pb sorption with decreasing pH and the rapid increase in the amount of Pb sorbed coincident to the formation of monovalent Pb-hydroxyl species are consistent with a cation exchange mechanism for Pb removal from solution by clay minerals. Table 8 exhibits further evidence that cation exchange is the principal mechanism for Pb removal by clay minerals.

The sorption maximums for $Pb(NO_3)_2$ solutions, computed from the slope of the Langmuir plots, for kaolinite and montmorillonite are 15.36 and 79.56 meq Pb^{++}/100 g clay, respectively. These values can be compared to the cation exchange capacity (CEC) values of 15.1 for kaolinite and 79.5 meq/100 g for montmorillonite that were determined by the ammonium acetate method and reported in Table 1. The CEC values are within 2% of the Pb sorption maximums computed from the Langmuir equation; i.e., Pb^{++} sorption is merely another method of measuring the cation exchange capacity of a clay.

Further evidence of a cation exchange mechanism is the reduction in Pb sorption in solutions containing 0.1 M NaCl and also as the total salt content of the two leachates studied increases. The decrease in Pb sorption is

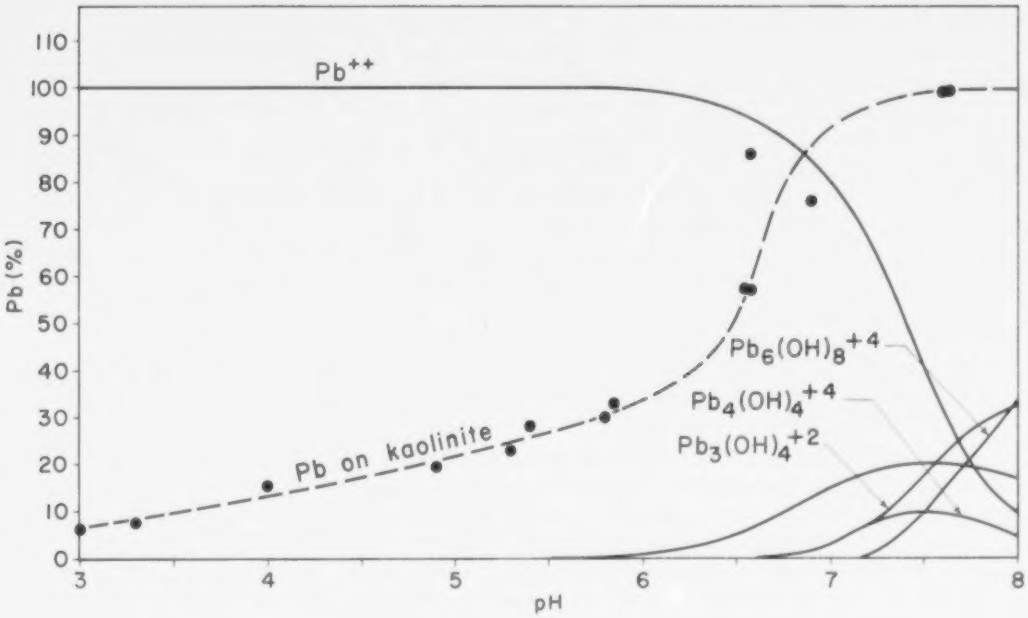

Figure 17. Distribution of Pb (II) species in 4 x 10^{-4} M $Pb(NO_3)_2$ and uptake by 0.1 g kaolinite from 60 ml of solution.

attributed to increasing competition for cation exchange sites by Na^+ in the 0.1 M NaCl solutions and to an increase in the divalent cation competition in the two leachates. For example, the Blackwell leachate contains much more Fe in solution than the DuPage leachate (Table 2). Such high levels of competing ions could account for the large reductions in Pb sorption observed in the presence of landfill leachate compared to the sorption in pure $Pb(NO_3)_2$ solutions.

The results for Pb sorption from leachate, plotted according to the Langmuir adsorption equation, show a distinct two-slope character. This shape of curve has been attributed to adsorption at sites of distinctly different energy (Griffin and Burau, 1974; Griffin and Jurinak, 1973). However, in the present study competition from other cations in solution seems to be responsible for the change in slope, because it was observed only in the multicomponent cation systems. Solutions of $Pb(NO_3)_2$ or NaCl did not exhibit the sharp change in slope for Pb sorption that was observed for the leachates.

One of the assumptions of the Langmuir equation is that the adsorbent surface is homogeneous with respect to the energy of the adsorption sites. However, in a multicomponent cation system the sites are occupied by cations with various retention energies relative to Pb; i.e., Pb can displace certain cations, such as Na^+, much more easily than it can replace cations such as Ca^{++}. This reaction is postulated to affect the shape of the adsorption isotherm by filling the lower energy sites preferentially; i.e., Pb first exchanges with a cation, or a group of cations, of similar exchange energy. This phase of the sorption is attributed to the initial slope of the Langmuir plot. As the concentration of Pb in solution is increased, the chemical potential gradient is increased until it is sufficient to initiate exchange of the cation, or group of cations, with the next highest energy of retention relative to Pb. This second energy level of exchange is postulated to produce the sharp change in slope of the Langmuir plots in the leachate solutions.

An explanation, other than competition for cation exchange sites, for the observed reductions in over-all Pb sorption is the tendency of Pb to form metal-organic complexes with the organic compounds present in landfill leachate. These organic-metal complexes can lower the activity of the Pb in solution, thus reducing the chemical potential gradient for sorption. Gadde and Laitinen (1973a) showed that Pb forms stable complexes with organic compounds found in soils and that these compounds were able to solubilize Pb present in different forms in the solid phase.

To determine the role of Pb-organic complexes in the observed Pb sorption reductions in leachates, the complexing capacity of Pb in the two leachates was measured.

In the DuPage leachate, the extent of complexation (ppm complexed) was found to be 22 ppm at a Pb concentration of 200 ppm. It is clear from the above data that only about 11% Pb is complexed, while it would take more than 50% complexation to explain the reduction in Pb sorption by an organic complexing mechanism.

The fact that formation of a Pb-organic complex cannot be used to explain more than a small fraction of the observed reduction in Pb sorption is emphasized by the results obtained from using Blackwell leachate. In this study it was found that addition of successive aliquots of Pb to the leachate gave approximately the same incremental response (μA-current) in the wave for free lead ion. Apparently up to 80 ppm total Pb, no complexation of Pb was observed. It was noted that Fe^{++} or its weak complex with leachate is presumed to have produced the large increase in polarographic current observed at a potential ~1.4 V. From the results of this study, it appears that Pb^{++} is either unable to compete with Fe^{++} or other cations present in large amounts in Blackwell leachate, or the leachate has little or no complexing capacity. The former explanation appears to be the more plausible.

The results of the above studies have led to the conclusion that Pb removal from solution is primarily an exchange-adsorption reaction that is affected by pH and ionic competition. The formation of Pb-organic complexes was concluded to be of secondary importance in landfill leachates due to competition from high concentrations of other cations. At pH values above 6, removal of Pb from solution by clay can be expected to increase substantially, owing either to increased adsorption of Pb-hydroxyl complexes or to formation of $PbCO_3$ in landfill leachates.

Disposal Site Design Application

An example of how the data from the study can be used is its application to the question posed at the beginning of the paper -- how thick a proposed clay liner must be to remove all Pb from landfill leachates, from industrial waste streams of similar ionic strength to the leachates (0.1 M NaCl), or $Pb(NO_3)_2$ solutions at various pH values and Pb concentrations. The results of the computations are presented in Table 9.

The table gives the thickness of a square meter of a 30% clay liner, packed to a bulk density of 1.60 g/cc, that contains enough clay to remove all the Pb from 762 liters (201 gal) of solution. This particular volume is the amount generated from a typical sanitary landfill containing municipal solid waste placed 3 meters (10 feet) deep and having an annual net infiltration of 254 mm (10 inches) (U.S.-EPA, 1974). The thicknesses of the clay liner given in the table, therefore, effect total removal of Pb for a year by a square meter of liner at the given concentrations of Pb and pH values. They are, of course, the minimum thickness possible since they represent an idealized situation. The actual thickness necessary in a field application will be somewhat greater to allow for non-equilibrium conditions, physical dispersion, diffusion, and the normal engineering safety factors.

The information compiled in Table 9 indicates that only relatively thin layers of clay, especially montmorillonite, are necessary for removal of Pb unless the pH values are very acid and the Pb concentrations are high. The high sorption capacity of clay minerals and the reversible nature of exchange adsorption reactions have important environmental consequences. Soils and surface waters may change in ionic composition or pH as environmental conditions change. A sudden decrease in pH may release large amounts of potentially toxic Pb into the aqueous phase, especially in places where $PbCO_3$ has

TABLE 9. THICKNESS (cm) OF A SQUARE METER OF A 30% CLAY LINER NEEDED TO REMOVE Pb FROM 762 LITERS (201 gallons) OF SOLUTION PER YEAR

	Pb Concentration								
	10 ppm			100 ppm			1000 ppm		
	at pH			at pH			at pH		
	3	5	8	3	5	8	3	5	8
KAOLINITE									
$Pb(NO_3)_2$	--	<1	--	5.3	1.8	<1	--	10.0	--
0.1 M NaCl	--	<1	--	--	2.3	--	--	15.5	--
DuPage	15.9	2.1	*	28.9	6.4	*	79.4	*	*
Blackwell	19.8	4.0	*	49.6	11.3	*	264.6	*	*
MONTMORILLONITE									
$Pb(NO_3)_2$	--	<1	--	--	<1	--	--	1.93	--
DuPage	9.9	1.8	*	13.2	3.7	*	18.0	*	*

*Precipitation as $PbCO_3$

accumulated. Cations, especially di- and tri-valent, compete with Pb and may exchange with it, thus allowing Pb to come into solution. These multiple interactions must be considered when a disposal site is designed and the environmental impact of Pb assessed.

SECTION 8

EXCHANGE-ADSORPTION OF Cu, Zn, AND Cd FROM DEIONIZED WATER AND LEACHATE SOLUTIONS BY CLAY MINERALS[1]

ABSTRACT

The effect of pH on the removal (exchange-adsorption by kaolinite and montmorillonite clay minerals plus precipitation) of copper, zinc, and cadmium in deionized water (pH range 4 to 6) and municipal leachate (pH range 2 to 8) solutions was studied. Solutions contained up to 1000 ppm Cu, Zn, or Cd. Families of removal versus pH curves were obtained that can be used to construct removal isotherms for specific pH values. With certain exceptions, very significant increases in the amounts removed from both solutions were observed as the pH rose in the pH ranges studied. Precipitation contributes significantly to removal of Cu from leachate above pH 5, Zn above 7, and Cd above 6.

Three different pH 5.0 removal isotherms are presented for deionized water solutions. These isotherms were constructed from removal curves obtained by different experimental methods which were shown to influence the interpretation of the results. The differences in the three isotherms are resolved by use of a Langmuir-type isotherm equation that was derived to express the simultaneous competitive adsorption of two cations. The equation reveals that, under certain conditions, the amount of exchange adsorption of a cation should be independent of its solution concentration. This proved to be true for the exchange adsorption of Cu, Zn, and Cd from deionized water solutions by the clay minerals at pH 5.0.

Isotherms of leachate removal at pH 5.0 were constructed and compared with the deionized water isotherms for the same pH. The amount of removal at pH 5.0 from leachate is significantly lower than it is from deionized water solutions because of competition from the other cations present in the leachate. Competition prevents the amount of exchange-adsorption at low concentrations from becoming independent of concentration. The leachate isotherms are specific for the leachate used and may not approximate the exchange-adsorption from another leachate of different ionic strength and composition.

The mobility of Cu, Zn, and Cd in soils or clay minerals is dependent upon the pH and ionic strength of the solution as well as on the CEC of the soils or clay minerals. The CEC value is of little importance at sufficiently

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high (above 7) pH values because precipitation is then more important than cation exchange in the removal of Cu, Zn, or Cd from solution.

INTRODUCTION

The results of chemical analyses of 20 municipal leachates have been reported by the U. S. Environmental Protection Agency (EPA, 1974). These analyses showed that leachate was similar to sewage sludge effluent with respect to its high content of organic matter, nitrogen, phosphorus, and potassium and also indicated levels as high as 10 ppm for Cu, 1000 ppm for Zn, and 17 ppm for Cd. The accumulation of these potentially toxic heavy metals in soils makes long-term application of municipal leachates to the land hazardous because Cu, Zn, and Cd enter the human food chain by accumulating in plants. However, a lack of basic data on the reactions of these metal ions with soil colloids in the presence of a complex solution matrix, such as leachate, hampers efforts to determine what levels of application can be tolerated without degradation or loss of the soil resource to food crop production.

The original purpose of this study was to measure the adsorption of Cu, Zn, and Cd by kaolinite and montmorillonite clay minerals from a landfill leachate at pH 5.0. However, the study was later expanded to investigate the adsorption of low concentrations of heavy metal ions by earth materials from deionized water solutions and their removal (adsorption plus precipitation) from a leachate in the pH range 2.0 to 8.0. The results of this study give insights into the mobility of Cu, Zn, and Cd in soils irrigated with leachates and can be applied to the design of clay liners for municipal and industrial waste disposal sites.

THEORETICAL

In any adsorption study, the amount adsorbed is usually measured as a function of adsorbate concentration in the medium surrounding the adsorbent. It is generally desirable to be able to fit the adsorption data to an adsorption isotherm equation so that "parameters" associated with the adsorption isotherm can be calculated for comparisons and correlation with other data.

The Langmuir (1918) equation is given as:

$$x/m = \frac{KbC}{1 + KC} \qquad \{7\}$$

where x/m = amount of adsorbate adsorbed per gram of adsorbent, C = the equilibrium ion concentration in solution, b = the adsorption maximum, and K = a constant related to the bonding-energy of the adsorbate to the adsorbent. This equation has been used extensively in studies of adsorption of ions from solution by soils and clay minerals. Eq. {7} can be rearranged into a linear form, where:

$$C/(x/m) = 1/(Kb) + C/b. \qquad \{8\}$$

The application of Eq. {8} to experimental data for Zn adsorption by soils (Shuman, 1975) has produced two linear portions of the plot. Following the lead of Syers et al. (1973), Shuman (1975) attributed this result to two types of adsorption sites. However, the adsorption model upon which Eq. {7} is based assumes that the surface of the adsorbent contains only one type of adsorption site. Therefore, there is no justification for arguing the existence of two sites on an adsorbent surface when a one-site model equation has been applied to the experimental data. Also, inspection of Eq. {7} shows that, at low concentrations, it reduces to:

$$x/m = KbC. \tag*{\{9\}}$$

Therefore, Eq. {8} has no significance at low concentrations, even though C/(x/m) values can be calculated and plotted. If a two-site adsorption model is to be discussed, then the following equation should be applied to the experimental data:

$$(x/m)_{total} = \alpha \frac{K_1 b_1 C}{1 + K_1 C} + (1-\alpha) \frac{K_2 b_2 C}{1 + K_2 C} \tag*{\{10\}}$$

where α = fraction of sites with bonding-energy coefficient K_1. In practice, Eq. {10} would be almost impossible to apply to experimental data.

The linear form of the Langmuir equation (Eq. {8}) holds best for the plateau region of the adsorption isotherm (high concentrations). This is true regardless of the equilibrium concentrations because the deviations from the linear plot occur as the equilibrium concentration approaches zero. A close look at Eq. {8} confirms this point. At, or near, the plateau region of the adsorption isotherm, (x/m) is about constant and, hence, the real plot is (C/constant) versus C, which must be a straight line. But at low concentrations, where (x/m) is increasing as C is increasing, values of C/(x/m) can change at a faster rate than they do at higher concentrations at which C is the only variable changing to an appreciable extent. Therefore, all Langmuir plots (Eq. {8}) will probably show two or more straightline segments if data points are obtained at sufficiently low and high concentrations.

The most important point ignored by the application of Eq. {7} to adsorption of cations from solution by soils and clay minerals is that the adsorption process is primarily one of cation exchange, and for every cation adsorbed one or more cations must be desorbed. The latter can then compete for adsorption sites. Boyd, Shubert, and Adamson (1947) developed an adsorption equation for the simultaneous competitive adsorption of two equally charged cations, A and B. By formal analogy with the Langmuir (1918) equation for adsorption from a binary gaseous mixture the following equation is obtained:

$$(x/m)_A = \frac{b\ K_A/K_B\ \ (C_A/C_B)}{1 + K_A/K_B\ (C_A/C_B)} \tag*{\{11\}}$$

The linear form of Eq. {11} is

$$\frac{C_A/C_B}{(x/m)_A} = \frac{K_B}{K_A\ b} + \frac{1}{b}\frac{C_A}{C_B}. \qquad \{12\}$$

Where the concentration of A is small compared to the concentration of B, so that adsorption of A does not produce a detectable change in the concentration of B (e.g., adsorption on a Ca-saturated clay from solutions with high Ca content), a plot of $C_A/(x/m)_A$ versus C_A should be linear. The plot should also be linear when $(x/m)_A$ approaches the cation exchange capacity (CEC), because C_B would then become a constant value and would not change as C_A changes. From Eq. {11} it can be seen that the amount adsorbed, $(x/m)_A$, must depend upon the ratio of the equilibrium concentrations of the exchanging cations and not upon the actual concentrations in solution. Where $C_B >> C_A$, $(x/m)_A$ will become a linear function of C_A, and when $C_A >> C_B$, $(x/m)_A$ will become a constant and independent of the concentration of A.

Equation {11} demonstrates that, under appropriate experimental conditions, the amount of exchange-adsorption should be independent of the solution concentration of the cation adsorbed. If it is desirable to study the migration of a cation through soils or clays by measuring its adsorption from a pure solution, then a fixed weight of soil sample and a fixed solution volume should be maintained throughout the concentration range being studied. However, it is not sufficient to measure the exchange-adsorption from pure cation solutions. For example, to determine how far the Cu, Zn, or Cd in 250 ml of 200 ppm deionized water solutions will migrate down a clay column the following procedure should be followed. One gram of clay is placed in the 250 ml of solution (initial concentration, C); adsorption will occur to give an equilibrium concentration, C_1. In the process, $(200-C_1) \times 0.25$ mg of cation is adsorbed and an equivalent number of moles of exchangeable cations on the clay will be desorbed. Hence, the solution phase will now contain a mixture of cations from which the amount of exchange-adsorption measured from a pure solution with a concentration of C_1. This process should be carried out stepwise, C to C_1, C_1 to C_2, ... , C_{n-1} to C_n, until $C_n \rightarrow 0$. Thus, the amount of adsorption from solution concentration C_1 will be dependent upon the initial concentration of the solution from which C_1 was derived.

EXPERIMENTAL

After pH adjustment, all clay-leachate or clay-deionized water suspensions in this study were shaken in a constant temperature bath at 25 ± 0.5° for at least 24 hours to insure complete equilibration. The equilibrium pH values of the clay suspensions were measured, the clay suspensions centrifuged, and the supernatant solutions were analyzed by atomic absorption spectroscopy for their Cu, Zn, or Cd concentrations. Blanks (i.e., no clay) of spiked leachate or deionized water solutions that had been prepared along with the clay suspensions also were analyzed to determine the initial Cu, Zn, or Cd concentrations present in the solutions. The amount of Cu, Zn, or Cd removed from solution by a given clay at a particular pH was calculated as the (initial equilibrium concentration) x (solution volume/sample weight) / 1000. The amount of Cu, Zn, or Cd removed from solution was plotted as a function of pH.

Three types of experiments were conducted on the removal of Cu, Zn, and Cd by the clay minerals from deionized water solutions of Cu, Zn, or Cd nitrates. In the first, 1.000 g of kaolinite or montmorillonite and 50-ml aliquots of the appropriate nitrate solution were placed into 125-ml Erlenmeyer flasks. The approximate concentrations chosen were: 25, 50, 100, and 200 ppm Cu and 10, 40, 200, and 400 ppm Zn for both kaolinite and montmorillonite; 100, 200, and 500 ppm Cd for kaolinite; and 100, 500, and 1000 ppm Cd for montmorillonite.

Three or four replicate clay suspensions were prepared for each concentration of Cu, Zn, or Cd. The pH values of the replicate clay suspensions were adjusted to various values in the pH range 4 to 6 with dilute HNO_3 or dilute NaOH solutions. The use of NaOH was avoided if possible because Na ions can compete for adsorption sites.

In the second type of experiment, the weight of the clay sample and/or the volume of solution were chosen so that the total amount of Cu, Zn, or Cd in solution per gram of clay would be a constant. The following quantities were used: about 12.5 mg of Cu/g of kaolinite (i.e., 250 ml at 25 ppm Cu/0.5g) at 10, 25, 125, 200, and 500 ppm Cu; about 62.5 mg of Cu/g of montmorillonite (i.e., 250 ml at 25 ppm Cu/0.10g) at 25, 125, and 500 ppm Cu; about 20.0 mg of Zn/g of kaolinite (i.e., 50 ml at 40 ppm Zn/0.10g) at 10, 40, 200, and 400 ppm Zn; about 100 mg of Zn/g of montmorillonite (i.e., 250 ml at 40 ppm Zn/0.10g) at 10, 40, 200, and 400 ppm Zn; about 25.0 mg Cd/g of kaolinite (i.e., 50 ml at 50 ppm Cd/0.10g) at 20, 50, 200, and 500 ppm Cd; about 125.0 mg Cd/g of montmorillonite (i.e., 250 ml at 50 ppm Cd/0.10g) at 50, 100, 200, and 1000 ppm Cd. Three or four replicate suspensions were prepared for each concentration of Cu, Zn, or Cd. The pH values of the replicate clay suspensions were adjusted to various values in the pH range 4 to 6.

In the third type of experiment, stepwise removal of Cu, Zn, or Cd from solution was studied. Some of the second type of experiment that used 250-ml solutions were taken as the first step in the third type of experiment. For the second step, the supernatant solutions from replicate clay suspensions in the first step were sampled for analysis and then mixed together. The combined solution was used with fresh clay samples to prepare three replicate clay suspensions which were adjusted to various pH values in the pH range 4 to 6. The supernatant solutions from the second step were used in a third step, etc.

Experiments on the removal of Cu, Zn, or Cd from leachate were carried out by pipeting 50-ml aliquots of leachate into 125-ml Erlenmeyer flasks. Either the leachate had been spiked with Cu, Zn, or Cd nitrates to give the desired concentration prior to the previous step, or 2.0 ml of an appropriate stock solution was pipeted into the flasks containing the 50-ml aliquots of non-spiked leachate. Several replicates were prepared for each concentration of Cu, Zn, or Cd used. The pH values of the replicate spiked leachate solutions were adjusted to various values throughout the pH range 2 to 8. Appropriately sized samples of either kaolinite or montmorillonite were then weighed out and transferred to the flasks. The weight of clay used was chosen so that the amount of Cu, Zn, or Cd removed from the leachate solutions could be determined with some precision from the difference between the initial and final solution concentrations.

It was discovered during preliminary experiments that, when the pH of a clay-leachate suspension was adjusted to a particular value, the pH of the suspension would rise on shaking and that the removal of Cu, Zn, or Cd increased with increasing pH. Thus, addition of the clay to the spiked leachate solutions after pH adjustments have been made avoids such potential problems as the possible irreversible removal of Cu, Zn, or Cd. The irreversible removal could occur if the pH of the prepared clay-spiked leachate suspension was high and the pH of the suspension was then adjusted to a much lower value. The experimental procedure used should produce true equilibrium removal data.

Several individual experiments also were carried out in which clay samples were placed in a mixture of 50-ml aliquots of pH 5 leachate or deionized water and 2-ml aliquots of different stock solutions. The pH of the resulting suspensions was repeatedly adjusted to 5.0 until equilibrium was obtained.

RESULTS AND DISCUSSION

The amount of Cu, Zn, or Cd removed from deionized water solutions was plotted versus pH. Except in certain cases, very significant increases in the amounts removed were observed as the pH rose in the range 4 to 6. The initial concentration of Cu, Zn, or Cd in solution, the weight of clay used, the final solution volume after pH adjustments, and the removal versus pH curves themselves can be used to construct "adsorption" or "removal" (adsorption plus precipitation) isotherms at different pH values by use of the following equation:

$$\text{Equilibrium concentration (ppm)} = \text{initial concentration (ppm)} - \frac{\text{Amount removed (mg/g)} \times \text{wt. clay (g)} \times 1000}{\text{Final solution volume (ml)}}. \quad \{13\}$$

Isotherms were calculated from the data recorded for the deionized water solutions at pH 5.0, and the results are shown as isotherm types I, II, and III in Figures 18 and 19.

The type I isotherms (Figs. 18 and 19) are those obtained when 1.00 g of kaolinite or montmorillonite was placed in about 50 ml of Cu, Zn, or Cd solutions. The total amounts of Cu, Zn, or Cd present in 50 ml of solution at different concentrations are given in Table 10. For kaolinite (CEC 15.1 meq/100 g), 75.5 μmoles of a divalent cation/g would be required for complete exchange; for montmorillonite (CEC 79.5 meq/100 g), 397.5 μmoles/g would be required for complete exchange. Thus, as indicated in Table 10, at low concentrations of Cu, Zn, or Cd, insufficient cations are present in 50 ml of solution for complete exchange of 1.00 g of clay (especially montmorillonite). The amount of Cu, Zn, or Cd that can be adsorbed is therefore necessarily limited by the number of Cu, Zn, or Cd ions initially present in solution. The number of Cu, Zn, or Cd ions actually adsorbed will depend on how well the desorbing Ca ions compete with the Cu, Zn, or Cd ions remaining in solution. The type I isotherms in Figures 18 and 19 specifically represent the

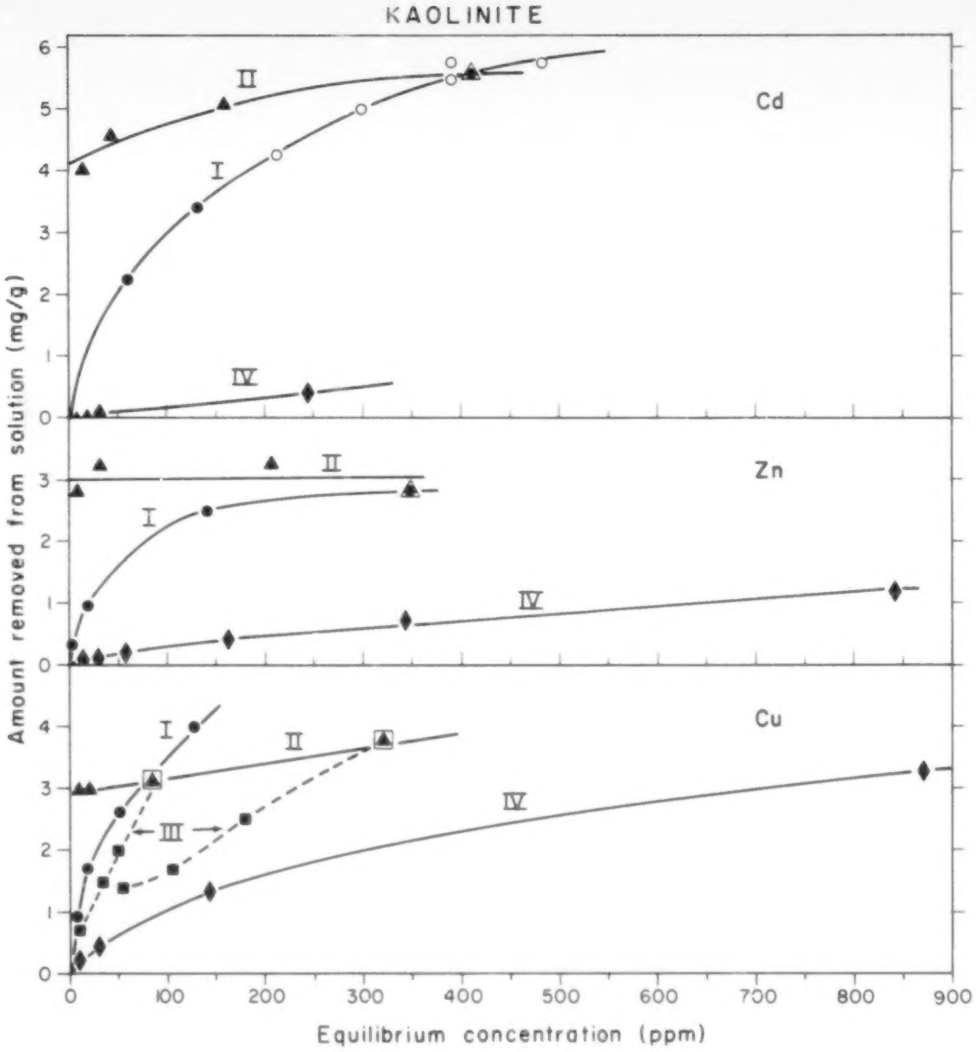

Figure 18. The amount of Cu, Zn, or Cd removed from solution per gram of kaolinite at pH 5.0 and 25° C, plotted as a function of the equilibrium concentration. Curve I - fixed weight clay/fixed solution volume; Curve II - total amount of clay exchangeable ions/total amount of Cu, Zn, or Cd ions in solution held about constant; Curve III - stepwise isotherms; Curve IV - DuPage leachate isotherms. Open symbol data points were obtained from clay suspensions adjusted several times to pH 5.0 instead of being calculated from removal curves at pH 5.0.

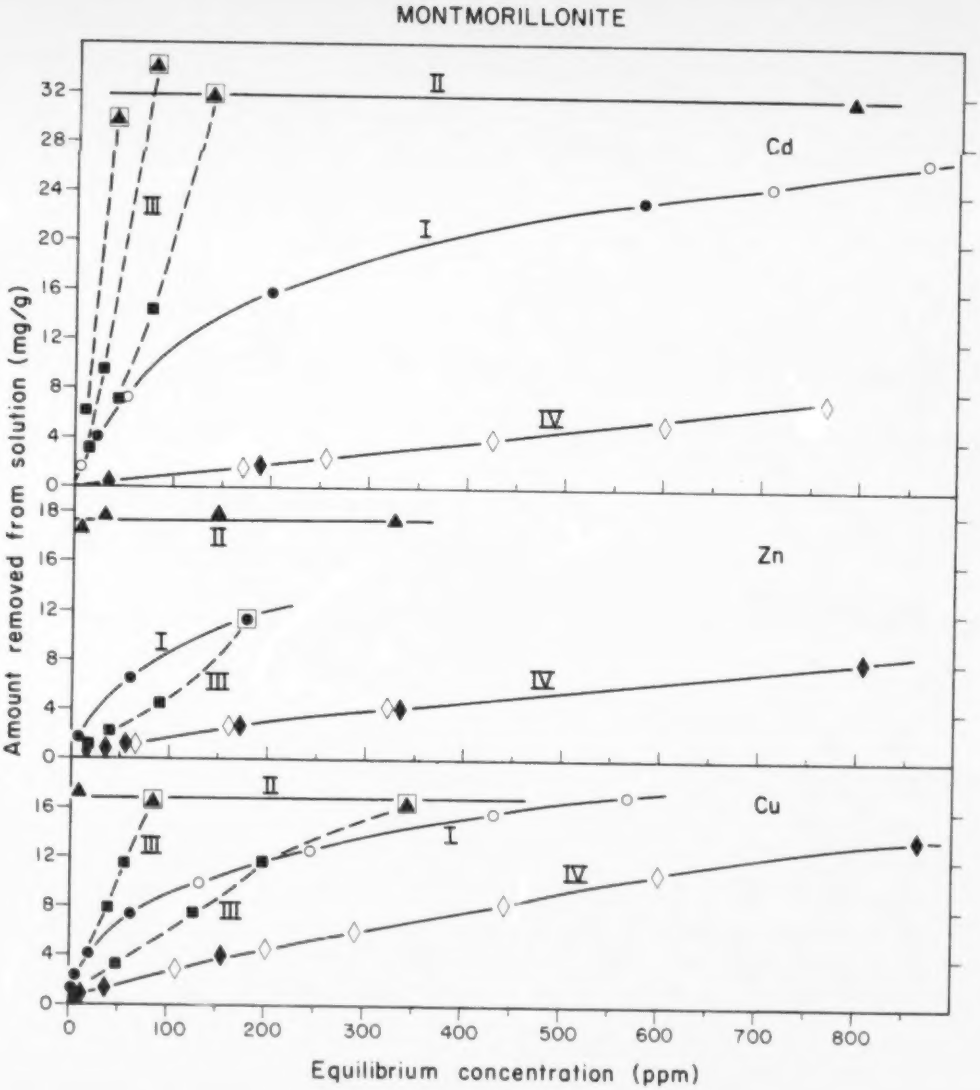

Figure 19. The amount of Cu, Zn, or Cd removed from solution per gram of montmorillonite at pH 5.0 and 25° C, plotted as a function of the equilibrium concentration. The labels I - IV and the open symbols have same meaning as in Fig. 18.

TABLE 10. TOTAL CONTENT OF Cu, Zn, OR Cd IN 50 ml OF SOLUTION

Initial concentration in solution	Cu	Zn	Cd
ppm	µmoles in 50 ml solution volumes		
4	3.15	3.06	1.78
10	7.87	7.15	4.45
25	19.7	17.9	11.1
40	31.5	30.6	17.8
50	39.4	38.2	22.2
100	78.7	76.5	44.5
200	157.4	153.0	89.0
400	314.8	306.0	178.0
500	393.4	382.5	222.5
1000	786.9	765.0	445.0

amount of Cu, Zn, or Cd adsorption by 1.00 g of clay from about 50 ml of solution.

The type II isotherms in Figures 18 and 19 were obtained when the weight of clay samples and/or solution volumes were adjusted so that the ratios (total number of Cu, Zn, or Cd ions)/(number of exchangeable cations on the clay samples) were held about constant (at least 2/1) and independent of the concentrations in the initial solution. Although, at equilibrium, the equilibrium concentration of Cu, Zn, or Cd (C_A) could not be considered to be much greater than the concentration of desorbing Ca ions (C_B), the ratio of C_A/C_B should be a constant and, hence, Eq. {11} says that $(x/m)_A$ should be constant and independent of C_A. This is shown by the type II isotherms in Figures 18 and 19. The "scatter" in the experimental data points for the type II isotherms is attributed to experimental errors due primarily to problems in measuring accurately the small changes in concentration that are due to adsorption. These errors must then be multiplied by large factors to compute the amount of metal removed per gram of clay.

The type I and II isotherms plotted according to the linear form (Eq. {8}) of the Langmuir equation (Eq. {7}) are shown in Figures 20 and 21. The Langmuir plots for the type I isotherms (1.00 g clay/50-ml solution) show a definite two-slope character (except the plot for Zn-kaolinite); in fact, three linear segments of the Langmuir plot appear to exist for the Cu-montmorillonite plot. The Langmuir plots (Fig. 21) of the type II isotherms for montmorillonite (Fig. 19; the total amount of Cu, Zn, or Cd initially present in solution /g clay was held about constant) show only a one-slope character throughout the concentration range investigated. The $C/(x/m)$ values definitely approach zero as the equilibrium concentration approaches zero. This is precisely what should occur if the competitive Langmuir equation (Eq. {11}) is valid, because Eq. {11} says that, if the equilibrium ratio C_A/C_B is constant, $(x/m)_A$ is independent of the actual concentration, and, therefore, as C_A approaches zero, $C_A/(x/m)_A$ must approach zero.

The Langmuir plots (Fig. 20) for the Cu and Cd type II isotherms with kaolinite (Fig. 18) do show a two-slope character. It was observed during the Cu adsorption experiments that the pH of the Cu-kaolinite suspensions in deionized water decreased when the flask was shaken, thereby indicating that hydrolysis of the Cu^{+2} ion was occurring in solution (i.e., $Cu^{+2} + H_2O = CuOH^+ + H^+$, etc.). Data on hydrolysis of cations that were assembled by Mesmer and Baes (1974) show that no appreciable concentrations of $CuOH^+$ or $Cu_2(OH)_2{}^{+2}$ will exist in solutions of low Cu concentration below pH 7, but, in the pH range 5 to 6, precipitation can occur from solutions of about 400 ppm Cu. Thus, precipitation is a reasonable explanation for the occurrence of the second slope in the Langmuir plot for Cu-kaolinite. Although similar arguments could be advanced for the Cd-kaolinite Langmuir plot, it appears from Mesmer and Baes (1974) that, in the range of Cd-concentrations used, hydrolysis and precipitation cannot be considered to be contributing factors to the "adsorption" of Cd by kaolinite around pH 5.0.

Shuman (1975) obtained two-slope Langmuir plots when he plotted Zn adsorption by Georgia soils data according to Eq. {8}. John (1972) found no significant correlation between the CEC values and Cd Langmuir adsorption

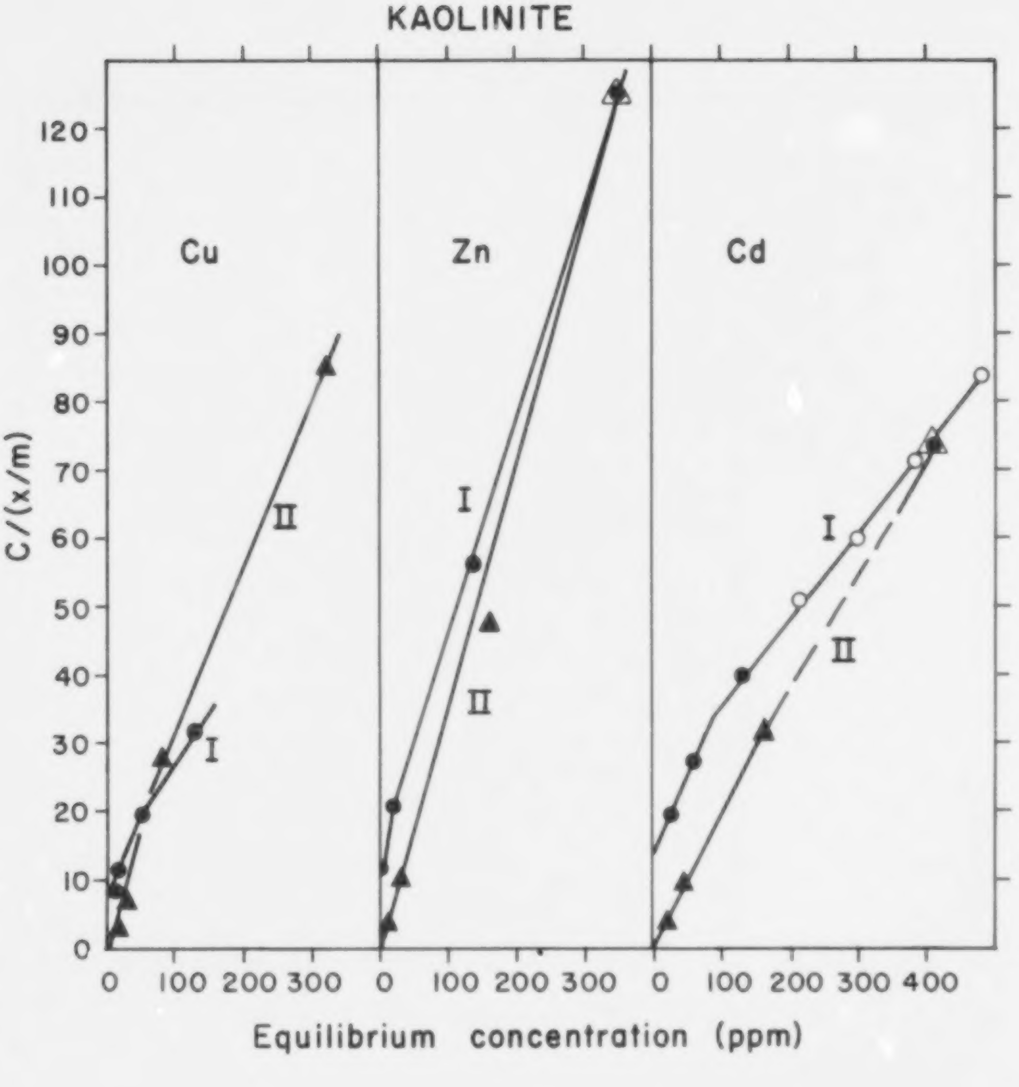

Figure 20. Cu, Zn, and Cd removal data for kaolinite in deionized water solutions at pH 5.0 and 25° C, plotted according to the Langmuir equation (Eq. 8). The roman numerals beside the plots indicate the corresponding isotherm in Fig. 18.

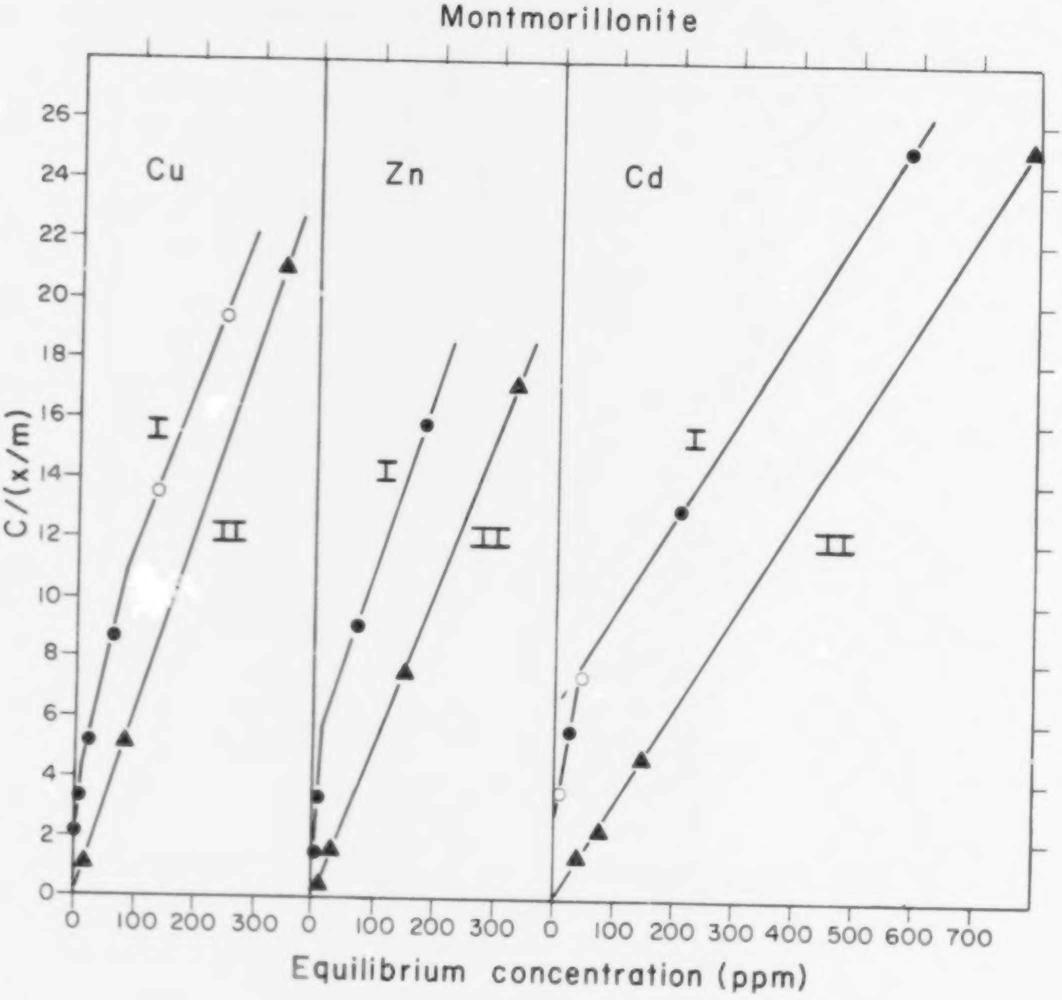

Figure 21. Cu, Zn, and Cd removal data for montmorillonite in deionized water solutions at pH 5.0 and 25° C, plotted according to the Langmuir equation. Numerals indicate corresponding isotherms in Fig. 19.

maximums for 30 different soil samples. Both Shuman (1974) and John (1972) used a fixed weight of soil and a fixed volume of solution in their adsorption measurements. The results of this study indicate that both Shuman (1974) and John (1972) would have obtained somewhat different results and conclusions if they had equilibrated their soil samples with sufficient solution volumes of low-Zn or Cd concentration so that the total Zn or Cd content of the solutions would exceed the CEC values of their respective soil samples. The appropriate solution volumes will necessarily depend on the CEC values of the soil samples (the larger the CEC, the larger the solution volume required) and what kind of exchangeable cations are present on the soil samples.

The type III isotherms in Figures 18 and 19 are "stepwise" isotherms. These isotherms show the competitive effect of the desorbing exchangeable cations initially present on the clay minerals on the removal of other heavy metal cations from solution. Thus, the type I and II isotherms in Figures 18 and 19 do not provide sufficient information to predict the migration of Cu, Zn, or Cd in pure solutions through soils or clays.

The adsorption data plotted by using the linear form (Eq. {12}) of the competitive Langmuir equation (Eq. {11}) are shown in Figures 22 and 23. It was assumed that the number of ions (presumed to be all Ca, which is more reasonable for kaolinite than for montmorillonite) desorbed from the clays into solution equals the amount of Cu, Zn, or Cd adsorbed from solution. It can be shown that C_A (ppm)/ΔC_A (ppm) = C_A(moles/l)/C_{Ca}(moles/l), where C_A = equilibrium concentration of Cu, Zn, or Cd and $\Delta C_A = C_{Initial} - C_A$, so that $(C_A/\Delta C_A)/(x/m)_A$ versus $(C_A/\Delta C_A)$ was plotted in Figures 22 and 23. For stepwise isotherms, the ΔC_A used included the ΔC_A values from previous steps. Although there is appreciable scatter to the data, reasonably straight lines (except for Cd-kaolinite), can be drawn through most of the data points, which include all data plotted for deionized-water solution isotherms I, II, and III in Figures 18 and 19. Some data points lie above the line drawn through the data points. At these data points, $C/\Delta C$ is generally small and the number of ions adsorbed (x/m) is limited by the total number of ions initially present in solution. Negative deviations from the main linear region can occur when Eq. {8} is used at low concentrations. Positive deviations from the main linear region can occur when Eq. {12} is used for small values of $C/\Delta C$.

The adsorption maximums calculated from the type II Langmuir plots in Figures 20 and 21 and the competitive-Langmuir plots in Figures 22 and 23 are given in Table 11.

The question arises as to why there is such poor correlation between the adsorption maximums calculated from the CEC values and the experimental adsorption maximums if cation exchange is the primary adsorption mechanism. Bittel and Miller (1974) have determined the selectivity coefficients for Cd/Ca on kaolinite and montmorillonite to be about one (i.e., Ca and Cd ions compete on about an equal basis for adsorption sites), but they do not specify a pH for their experimental measurements. The data obtained in this study indicate that the selectivity coefficients for Cu, Zn, and Cd on Ca-saturated kaolinite and montmorillonite are less than one at pH 5 and ap-

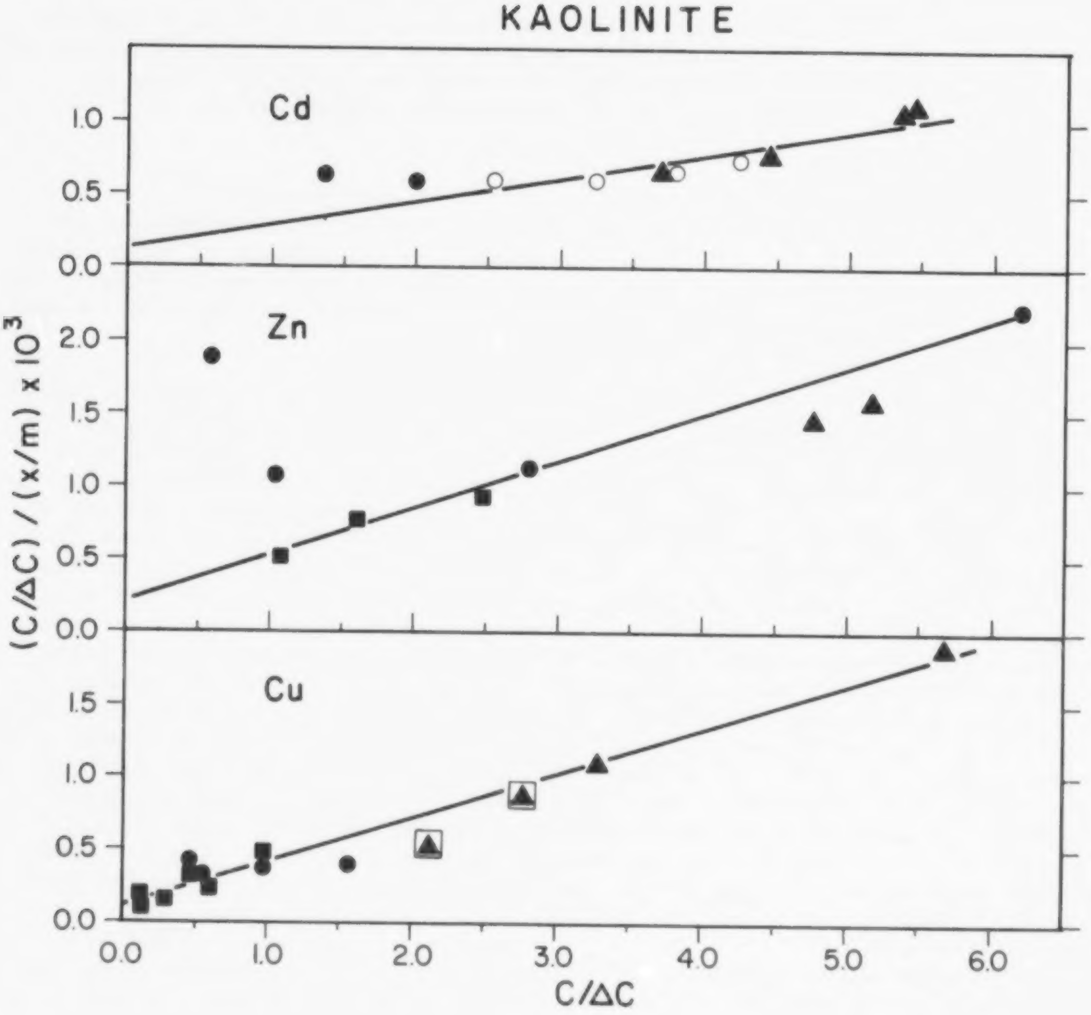

Figure 22. Cu, Zn, and Cd removal data for kaolinite in deionized water solutions at pH 5.0 and 25° C, plotted according to the competitive Langmuir equation (Eq. 12). The data point symbols correspond to those used in Fig. 18.

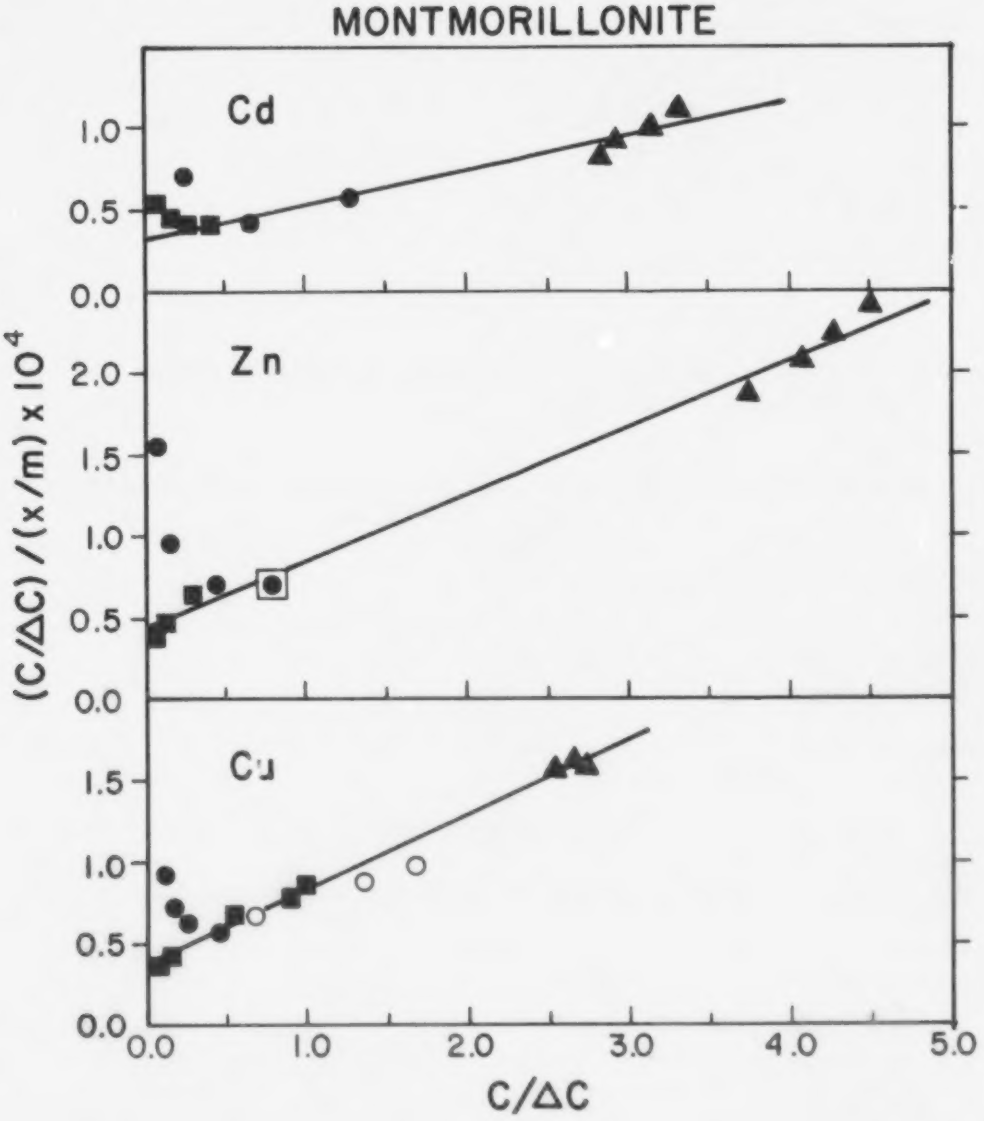

Figure 23. Cu, Zn, and Cd removal data for montmorillonite in deionized water solutions at pH 5.0 and 25° C, plotted according to the competitive Langmuir equation (Eq. 12). The data point symbols correspond to those used in Fig. 19.

TABLE 11. COMPARISON OF LANGMUIR ADSORPTION MAXIMUMS IN DEIONIZED WATER WITH CEC VALUES

Source	Cu		Zn		Cd	
	K*	M†	K	M	K	M
	mg/g					
II - Langmuir plots (Figs. 21 and 22)	3.08	18.5	2.86	19.2	5.0	31.2
Langmuir plots (Figs. 23 and 24)	3.33	21.0	3.00	23.6	-	50.0
Calc. from CEC values - Table 1	4.80	25.3	4.94	26.0	8.45	44.8

*Kaolinite
†Montmorillonite

proach one at higher pH. Therefore, the experimental adsorption maximums for Cu, Zn, or Cd would not approach the CEC values until the equilibrium ratio C/C_{Ca} was larger than was the case in any of our experiments. Because the adsorption of Cu, Zn, or Cd is pH-dependent, the adsorption maximums will, of course, show definite pH-dependence. Prior to the onset of precipitation, which is dependent on both concentration and pH, decreasing competition from H^+ and increasing concentration of hydrolyzed ions (e.g., $Cu_2(OH_4)^{+2}$, $ZnOH^+$, and $CdOH^+$) are possible reasons for the "adsorption" to increase as pH increases.

Curves for pH versus the removal of Cu, Zn, or Cd from leachate by kaolinite and montmorillonite are shown in Figures 24 and 25, respectively. The data listed beside each curve and in the figure captions were used in Eq. {13} to calculate the type IV isotherms at pH 5.0, which are shown in Figures 18 and 19. This was done so that direct comparisons could be made with the deionized-water isotherms. Figures 18 and 19 show that the removal from leachate is appreciably lower than the removal from deionized-water solutions. Boyd, Shubert, and Adamson (1947) gave a general expression for the exchange adsorption of a cation, A, from a mixture of equally charged cations in solution, which is as follows:

$$(x/m)_A = \frac{b\ K_A\ C_A}{1 + \sum_{\mathrm{all}_j} K_j\ C_j}. \qquad \{14\}$$

Equation {14} says that the exchange adsorption of any one cationic species at constant concentration will decrease as the concentrations of other cationic species increase. Thus, from solutions of constant ionic strength, in which the total ionic content is large compared to the total number of exchangeable cation on any soil or clay mineral sample placed in that solution, the amount of Cu, Zn, or Cd removal cannot approach the CEC of the soil or clay mineral at low concentrations, as is true in the case of exchange-adsorption from deionized water (i.e., increasing solution volume will usually not affect the equilibrium concentration ratio of the cation of interest to the other cations in solution to any appreciable extent). Only when the concentrations of Cu, Zn, or Cd in solution exceed the combined concentrations of all other cationic species in solution will the amount of exchange-adsorption of Cu, Zn, or Cd approach the CEC of the soil or clay mineral sample being tested. In practice, except at very low pH, precipitation of Cu, Zn, Cd and other heavy metal ions as hydroxides and/or carbonates will occur at moderate concentrations so that precipitation rather than cation exchange adsorption can become the principal mechanism for the removal of heavy metal ions from solution.

The sharply rising portions of the removal curves shown in Figures 24 and 25 can easily be interpreted, with the aid of information assembled by Mesmer and Baes (1974), as being caused primarily by precipitation of Cu, Zn, or Cd carbonates, hydroxides, or hydroxide-carbonates. Removal of Zn and Cd from the leachate by both kaolinite and montmorillonite is greatly reduced compared to their removal from deionized water solutions at pH 5.0. The amount of Zn and Cd removed is reduced proportionally about the same for both

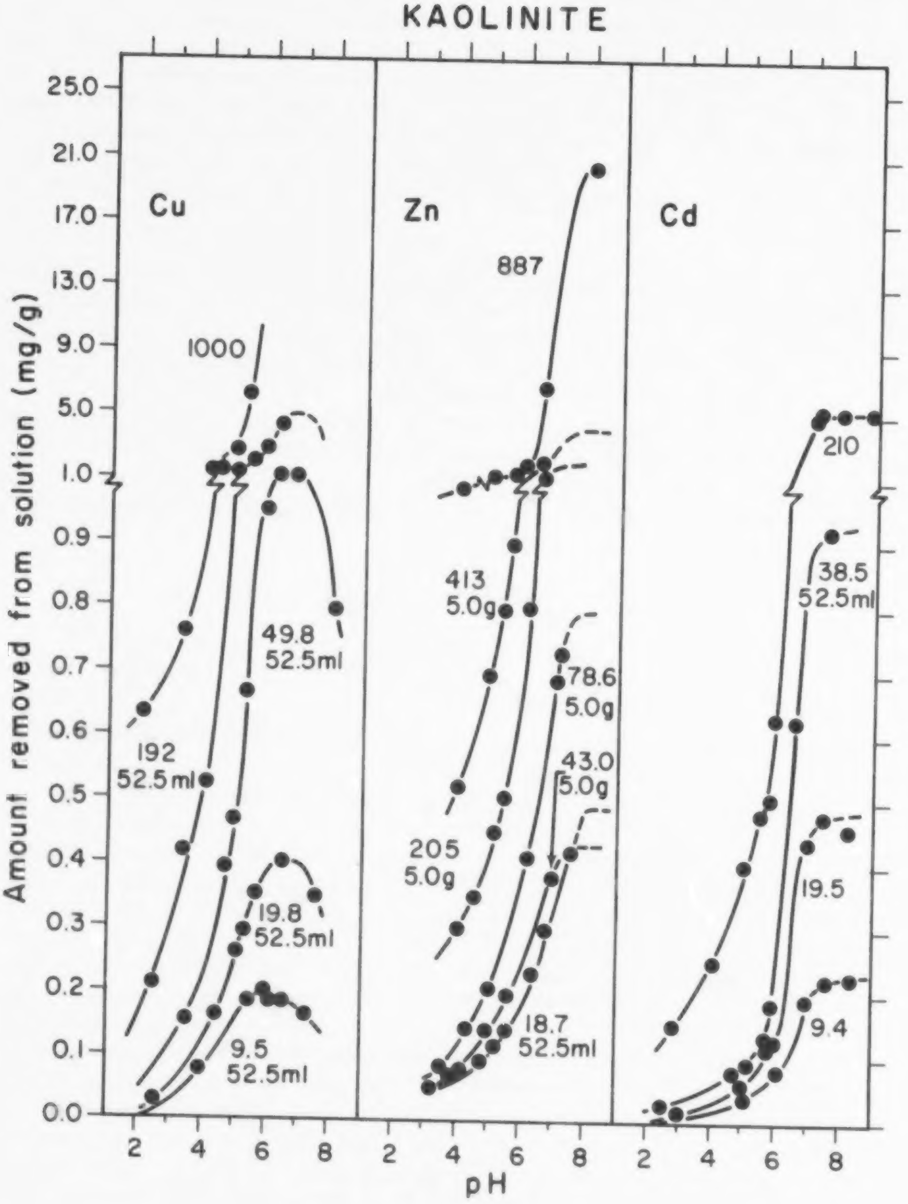

Figure 24. The amount of Cu, Zn, or Cd removed from DuPage leachate solutions by kaolinite at 25° C, plotted as a function of pH. The plots are labeled with the initial solution concentration (ppm) of Cu, Zn, or Cd from which each plot was obtained. Unless otherwise indicated, 2.0 g of clay and a total leachate solution volume of 50.5 ml were used to obtain each data point.

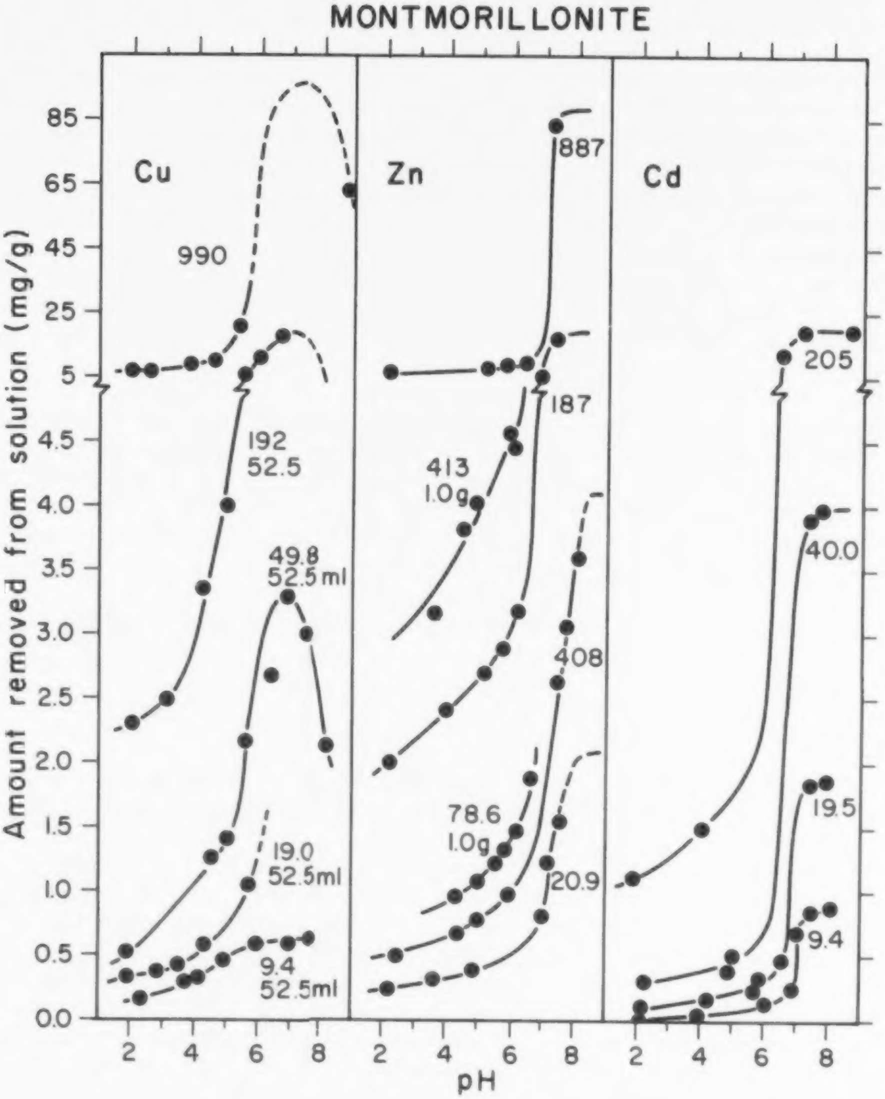

Figure 25. The amount of Cu, Zn, or Cd removed from DuPage leachate solutions by montmorillonite at 25° C, plotted as a function of pH. The plots are labeled with the initial solution concentration (ppm) of Cu, Zn, or Cd from which each plot was obtained. Unless otherwise indicated, 0.5 g of clay and a total leachate solution volume of 50.5 ml were used to obtain each data point.

kaolinite and montmorillonite, but the reduction in the amount of Cu removed from the leachate is appreciably greater for montmorillonite than for kaolinite. This can readily be explained on the basis that the Cu-leachate isotherms represents a combination of exchange-adsorption and precipitation. The amount of Cu removed by precipitation, for example 1 mg/g, will be about the same for leachate solutions at pH 5, whether kaolinite or montmorillonite is present in solution. However, the 1 mg/g represents about 20% of the CEC for kaolinite, while it represents only about 4% of the CEC for montmorillonite. The decrease in removal from leachate, therefore, appears much greater for montmorillonite than for kaolinite. The actual decrease in Cu exchange-adsorption is probably proportionally the same for both clays. The removal of Cu from leachate reaches a maximum about pH 7 (Figs. 24 and 25) and then decreases for pH values above 7. This behavior is due to the amphoteric character of $Cu(OH)_2$ precipitates, which redissolve in basic solutions by forming $Cu(OH)_3^-$, etc. ions.

The amount of Cu, Zn, or Cd removed from leachate has no significant apparent dependence on leachate volume, as can be seen from the leachate isotherms (Figs. 18 and 19), on which data points obtained for different clay sample weights but constant leachate volumes have been plotted on one isotherm curve. However, the amount removed could become dependent on the leachate volume if the clay sample is very large.

Equation {14} implies that at some given ionic strength, where

$$\sum_{\text{all}_j} K_j C_j$$

is about constant and large compared to one, $(x/m)_A$ = Constant x C_A. The isotherms for Cd (Figs. 18 and 19) are linear to quite high concentrations.

The isotherms for Cu, Zn, or Cd removal from leachate were not plotted according to the linear form of a Langmuir adsorption isotherm equation, although, most assuredly, straight line plots would have been obtained and "adsorption" maximums could be calculated. The reasons for not plotting them were, first, none of the leachate isotherm plots have really reached the plateau region in the concentration range studied (up to 1000 ppm). Second, any adsorption maximums calculated from the Langmuir plots would be somewhat meaningless because the amount of exchange-adsorption from leachate is limited by competition, owing to the high ionic strength of the leachate and not because all the adsorption sites have been occupied by Cu, Zn, or Cd ions, as is implied with a Langmuir adsorption maximum. Third, if an adsorption maximum is calculated from the rising part of an isotherm, it represents the amount adsorbed at some higher hypothetical concentration that may or may not lie on the real adsorption isotherm. Finally, our purpose was to determine the maximum amount of Cu, Zn, or Cd that can be removed by kaolinite or montmorillonite from leachate at any particular concentration up to approximately 1000 ppm. As we have seen for removal from deionized water, with appropriate experimental conditions, the amount removed is independent of concentration and is proportional to the CEC values of the clays. It would presumably approach the CEC at higher (volume)/(weight of clay) ratios. But, with leachate, the ionic strength is not a variable to be adjusted and the conditions cannot be created where at low concentrations of Cu, Zn, or Cd the ratio of the (equilibrium concentration of Cu, Zn, or Cd)/(concentration of other cations) is large. The maximum amount removed must then be a function of the ionic strength of the leachate, the CEC of the clay sample, and pH of the leachate. Therefore, the maximum amount removed at any concentration and pH from leachate (or for that matter any solution) is simply the value read from the removal isotherm itself at the concentration of interest.

SUMMARY AND CONCLUSIONS

Under appropriate experimental conditions, the amount of Cu, Zn, or Cd exchange-adsorbed from deionized water by purified kaolinite and montmorillonite clay minerals is independent of the equilibrium concentration of Cu, Zn, or Cd. However, the maximum amount of Cu, Zn, or Cd adsorbed in our experiments was related to, but not equal to, the CEC values of the clay minerals, probably because the desorbing Ca ions effectively competed with the Cu, Zn, or Cd ions present in solution. If cation-exchange adsorption experiments are carried out at constant (solution volume)/(sample weight) ratios for Cu, Zn, or Cd in deionized water, the amount of adsorption is necessarily limited by the total amount of Cu, Zn, or Cd that was initially present in solution at low concentrations. Therefore, the isotherm obtained is really a plot of the amount of Cu, Zn, or Cd removed by a fixed weight of sample from a fixed volume of solution versus concentration. At low concentrations a different isotherm can be obtained simply by using a different constant (solution volume)/(sample weight) ratio in the experiments. To properly simulate field conditions, soil samples must be equilibrated with sufficient solution volumes so that the total metal ion content of the solutions exceeds the adsorption capacity (CEC values) of the respective soil samples. The appropriate solution volumes will necessarily depend on the CEC of the soils and the kind of exchangeable cations present on the soil samples.

If it is desirable to study the migration of Cu, Zn, or Cd from deionized water through soils or clays by means of batch experiments, the experiments can be carried out stepwise (i.e., repeated treatments of a solution with new soil or clay samples) for each initial solution concentration tested. That is necessary because of the increasing concentration of exchangeable cations in solution as exchange-adsorption of an individual cation from solution occurs stepwise towards zero. This is not a particular problem in high ionic strength solutions such as landfill leachate as discussed below.

The three different types of isotherms obtained for the same range of Cu, Zn, or Cd concentration are easily interpreted in terms of a cation exchange-adsorption mechanism. Also, the correct "Langmuir" isotherm equation to apply to exchange adsorption data is Eq. {11}, which covers the simultaneous competitive adsorption of two cations, and not Eq. {7}, which is for a single cation. Although strict application of Eq. {11} requires the exchangeable cations on the adsorbent to be homoionic, the principal conclusion that "under appropriate conditions" the amount of exchange-adsorption is independent of concentration will apply, regardless of the number of exchangeable cations on the adsorbent.

The adsorption of Cu, Zn, or Cd from leachate by kaolinite and montmorillonite clay minerals is presumed to occur via a cation exchange mechanism, but, because the high ionic strength of the leachate is relatively unvariable in the adsorption experiments, the amount adsorbed does not become independent of the concentration of Cu, Zn, or Cd in the leachate. Thus, there is no way to predict the maximum amount of Cu, Zn, or Cd that will be adsorbed from a given leachate by a given soil or clay mineral, at a given pH and at some concentration without actually measuring it. At pH 5.0, precipitation of Cu as a hydroxide-carbonate makes a very significant contribution to the total amount of Cu removed by kaolinite but, because montmorillonite has a higher amount of exchange-adsorption, the contribution of precipitation to the total amount of Cu removed by montmorillonite is less significant. If the pH of the leachate is lower than about 6.5, precipitation does not make a significant contribution to the total amount of Zn and Cd removed by kaolinite and montmorillonite.

The mobility of Cu, Zn, and Cd in soils or clay minerals is similar to Pb and is dependent upon solution pH and ionic strength as well as on the CEC of the soils or clay minerals. This is of little importance at sufficiently high (above 7) pH values, because precipitation is then more important than cation exchange in the removal of Cu, Zn, or Cd from solution. However, the mobility of Cu would apparently reach a minimum at pH 7 and would subsequently increase at pH values above 7. At pH 5, Cu, Zn, and Cd in leachate will be quite mobile in soils or clay minerals with low CEC values, especially when the ionic strength of the leachate is high. Thus, if adsorption data at pH 5.0 is obtained either from a leachate very high in ionic strength or from a low CEC soil or clay mineral, and the mobility of Cu, Zn, or Cd is calculated, it can be stated that for higher pH values, for higher CEC values, and/or for leachates low in ionic strength, the mobility would be less than it is at pH 5.0. These facts add a built-in safety factor to estimations of adsorption and/or mobility.

Treatment of a soil with a waste stream or leachate will alter the exchangeable cation distribution of the soil; for example, a high Ca soil will become a high Na soil if treated with a high Na-content waste stream or leachate. Thus, other potential problems may be created that must be evaluated in addition to the problem of heavy metal toxicity to plants or heavy metal accumulation in the food chain when waste streams or leachates are disposed of on agricultural land.

SECTION 9

EFFECT OF pH ON CHROMIUM ADSORPTION FROM LANDFILL LEACHATE BY CLAY MINERALS[1]

ABSTRACT

The adsorption of Cr(VI) and Cr(III) species by kaolinite and montmorillonite clay minerals was found to be highly dependent upon the pH of the clay suspensions and the physical-chemical properties of the clay minerals. Solution ionic strength was found to be of secondary importance to estimations of Cr(VI) and Cr(III) adsorption.

No precipitation of Cr(VI) was detected in the pH range 1.0 to 9.0. Precipitation of Cr(III) as an amorphous hydrated hydroxide starts to occur above pH 4.5.

The adsorption of Cr(VI) from a given solution decreased as pH increased. The Cr(VI) species distribution indicated that the $HCrO_4^-$ ion was the Cr(VI) species predominantly adsorbed. Montmorillonite adsorbed about four times more Cr(VI) than kaolinite under similar conditions of pH and ionic competition. Contrary to expectations, less Cr(VI) was adsorbed from pure K_2CrO_4 solutions than from leachate solutions.

The adsorption of Cr(III) increased as the pH of the suspensions increased. At pH 2.5, the amounts of Cr(III) adsorbed were consistent with a cation exchange mechanism involving Cr^{3+} ions. As the pH is raised to 4.0, the amounts adsorbed correspond to cation exchange adsorption of the hydrolized Cr(III) species, $Cr(OH)_2^+$ and $Cr_6(OH)_{15}^{3+}$. The adsorption of Cr(III) is 3% to 14% lower in leachate than in pure $Cr(NO_3)_3$ solutions.

For a given type of clay, about 30 to 300 times more Cr(III) than Cr(VI) is adsorbed depending upon pH and the ionic competition in solution. The results of the study suggest that landfill disposal of Cr(VI) wastes represents a potential pollution hazard due to its high mobility in earth materials and that safe disposal may require conversion of Cr(VI) wastes to Cr(III) before disposal in landfills.

INTRODUCTION

Efforts to effectively dispose of most industrial heavy metal wastes without polluting the environment have thus far proved unfruitful. Traditionally, rivers or lakes have been used for the disposal of these potentially hazardous discharges. Industrial plants have also disposed of their wastes through recharge basins or diffusion wells (Welsch, 1955), and into sewer systems (Nassau County, N. Y., Department of Public Works Sewer Regulations, 1955). All of these disposal methods can contribute to contamination of surface and ground water (Davids and Lieber, 1951). To minimize the problems caused by heavy metal wastes in sewage treatment, laws have been enacted in some northern Illinois counties forbidding the disposal of such wastes into sanitary sewers. That prohibition has increased the pressure for permission to dispose of these wastes in the available sanitary landfill sites. However, unless specially designed, sanitary landfills also are a potential source of surface and ground-water pollution (Walker, 1969). For that reason a demand has arisen for information about the capacity of earth materials to adsorb heavy metals from landfill leachates (Fuller, 1975).

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[1] Authors: R. A. Griffin, Anna K. Au, and R. R. Frost

Chromium compounds are widely used in the leather, textile, chemical manufacturing, metal finishing, and other industries. Approximately 30,000 tons of chromium-bearing wastes are discharged annually from the metal finishing industries alone (U.S.-EPA, 1973), and problems of environmental pollution have arisen. Chromium (VI) contamination of the village wells in Douglas, Michigan, was reported in 1947 (Davids and Lieber, 1951), and as early as 1952 chromium was found in high concentration in the ground water of Nassau County, New York (Welsch, 1955).

In trace amounts, chromium is an essential element in the diet of some animals and, presumably, human beings. However, at sufficiently high concentrations, all compounds of chromium are toxic (Smith, 1972). The valence state of chromium has a considerable influence on its toxicity. It is well established that Cr(VI) compounds are the most toxic and are usually irritating and poisonous to all tissues (Baetjer, 1956).

Thus far, the distribution and impact of chromium on aquatic ecological systems have not received extensive study, so that relatively little is known about the transfer of the metal from waste streams to earth materials and then to living systems. Because knowledge of the chromium-leachate system is scant, the present study was conducted to investigate the effect pH has on Cr(VI) and Cr(III) adsorption by clay minerals plus precipitation in deionized water and municipal leachate solutions. It was also desired to gain insight into the factors that affect the mobility of chromium as it passes through soils or clay-mineral layers. These soil or clay layers may be potentially useful as liners for waste disposal sites.

EXPERIMENTAL

Various concentrations of Cr(VI) in deionized water and DuPage leachate were prepared using potassium chromate (K_2CrO_4), and 50-ml aliquots were pipetted into Erlenmeyer flasks containing either 3 g of montmorillonite or 5 g of kaolinite. The weight of clay used was chosen so that the amount of Cr removed from the solutions could be determined with some precision from the difference between the initial and final solution concentrations. Several replicate suspensions for each concentration were prepared, and their pH values were adjusted with either HNO_3 or NaOH to various values in the pH range 1.0 to 9.0.

In preliminary experiments, the amount of Cr(VI) adsorption was found to decrease as pH increased, and pH values of the Cr(VI)-clay suspensions rose when the flasks were shaken. Also, apparent irreversible Cr(VI) adsorption occurred if the Cr(VI)-clay suspensions had been equilibrated at one pH value and again equilibrated at a higher pH value. Therefore, the flasks were shaken for about 2 weeks in a constant temperature bath at 25 ± 0.5° C; the pH values of the clay suspensions were measured each day, and acid or base was added when necessary to maintain the initial pH value. At least one day after the final pH adjustment, the pH values were recorded and the suspensions were centrifuged. The supernatant solutions were then decanted into plastic bottles and their pH adjusted to 2.0 to prevent any Cr adsorption by the container. The equilibrium Cr concentrations C_{Eq} (ppm) in the supernatant solutions were determined by atomic absorption spectroscopy. The initial Cr concentration (C_I) in ppm was determined by analyses of blank sample, i.e., sample without clay, prepared at the same time as the clay suspensions. In our experiments, C_I concentrations ranging from 5 to 300 ppm Cr as Cr(VI) were used.

The amount of Cr(VI) adsorbed (x/m) in mg/g clay at a given pH was calculated as $(C_I - C_{Eq}) \times V_E/1000$ where V_E = final solution volume (ml)/weight of clay sample (g). The amount of Cr(VI) adsorbed by a fixed amount of clay from a given C_I solution at various pH values was plotted against the pH values to obtain an adsorption-pH curve.

The experimental procedures for the Cr(III) adsorption studies were similar to those used in the Cr(VI) experiments. It was determined that 0.100 g of the clay minerals would give the desired precision in determining the change in Cr(III) concentrations at equilibrium. Chromium (III) nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) was used as a source of Cr(III). The study of Cr(III) adsorption was generally limited to the pH range of 1.5 to 4.5 because of Cr(III) precipitation around pH 5. Because of the precipitation, the pH of the leachate was adjusted to about 4 prior to "spiking" with Cr(III). An initial Cr(III) concentration range of 30 to 800 ppm was chosen for the experiments.

RESULTS AND DISCUSSION

Adsorption isotherms can be calculated from a family of adsorption-pH curves at different pH values. The amount of Cr adsorbed (x/m) in mg/g clay at a particular pH value is read from an adsorption-pH curve for a particular C_I and the equilibrium concentration, C_{Eq}, in ppm is calculated from the following equation:

$$C_{Eq}\ (\text{ppm}) = C_I\ (\text{ppm}) - \frac{(x/m) \cdot 1000}{V_E} \qquad \{15\}$$

where all the parameters are as previously defined.

Interpretation of the adsorption data was aided by application of the Langmuir equation (1918). In the derivation of the Langmuir equation it is assumed that (a) the surface is energetically homogeneous, (b) the adsorbate-adsorbate interaction on the surface is negligible, and (c) the adsorbed molecules do not influence neighboring sites. The Langmuir adsorption equation in its linear form is:

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \qquad \{16\}$$

where C is the equilibrium concentration of the ion, x is the amount adsorbed, m is the mass of adsorbent, b is the adsorption maximum, and k is a constant that relates to the energy of adsorption.

Chromium (VI) Adsorption

No precipitation of Cr(VI) was observed in the pH range 1.0 to 9.0. Families of Cr(VI) adsorption-pH curves are presented in Figures 26 and 27. Several characteristics of Cr(VI) adsorption by the clays appear. First, the adsorption of Cr(VI) decreases as pH increases. Second, Cr(VI) is not adsorbed by the clays near pH 8.5 and above. Third, the amounts of Cr(VI) adsorbed are small compared to the amounts of exchangeable cations on the clay samples.

Diagrams showing the distribution of Cr(VI) species covering the experimental concentration range are presented in Figure 28 and were calculated by using the constants given in Butler (1964). Noteworthy is the rapid decrease in the fractions of $HCrO_4^-$ and $Cr_2O_7^{2-}$ species above pH 5 and the corresponding increase in the fraction of CrO_4^{2-} species, which become the principal species present in solution at about pH 8.5 (Fig. 28). Below pH 2 the fraction of $HCrO_4^-$ ions decrease rapidly as the fraction of H_2CrO_4 species increases.

The behavior of the Cr(VI) adsorption-pH curves in Figures 26 and 27 implies that the $HCrO_4^-$ ion is the principal ion being adsorbed by the clay minerals. Conversely, the lack of adsorption at pH values above 8.5 indicates that the CrO_4^{2-} ion is not adsorbed at all by either of the two clays. The mechanism of Cr(VI) adsorption by these clay minerals apparently cannot neutralize the two negative charges present on the CrO_4^{2-} ion. On the other hand, $Cr_2O_7^{2-}$ ions may be adsorbed at low pH values because of its more open structure, $CrO_3^- - O - CrO_3^-$, which places the two negative charges an appreciable distance apart, as opposed to charges on adjacent oxygens that occur in the CrO_4^{2-} structure. The charge separation on the $Cr_2O_7^{2-}$ ion may allow it to act essentially as two monovalent ions, with each negative charge fulfilling an adsorption site or one negative charge fulfilling an adsorption site and the other negative charge being neutralized by a cation in solution. If the distribution of Cr(VI) species in solution is the only factor governing adsorption of Cr(VI) over the pH range 2 to 5, a plateau should be observed in the Cr(VI) adsorption-pH curves; however, the adsorption of Cr(VI) continues to rise with decreasing pH to a pH value around 2. Therefore, in the low pH range the pH probably modifies the structures of the clay minerals to permit increased Cr(VI) adsorption to occur. Dissolution of clay minerals is known to occur at low pH levels (Hofmann et al., 1956). This can alter the surface structure and surface area of the clays, resulting in changes in their adsorption characteristics as the pH is lowered.

Adsorption isotherms were constructed from the Cr(VI) adsorption-pH

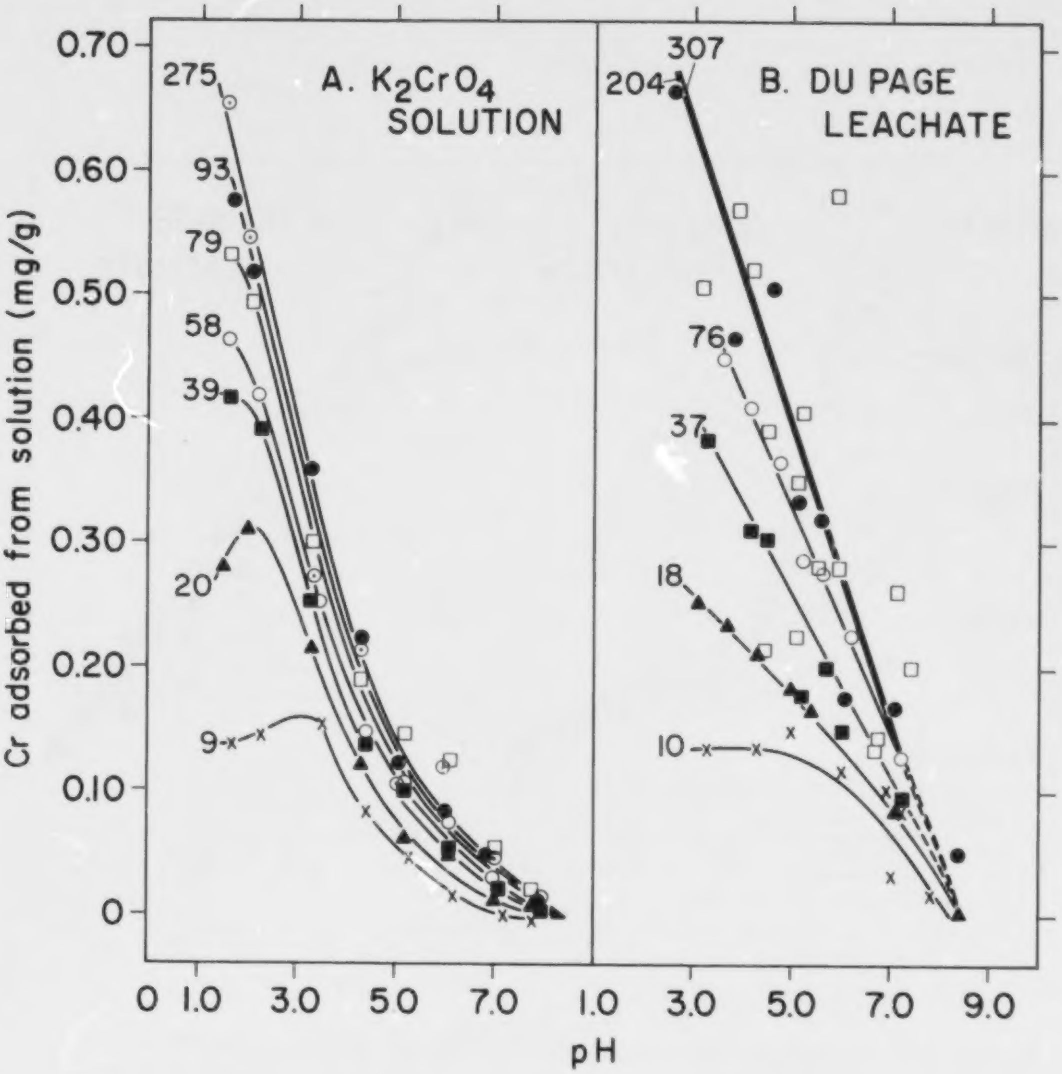

Figure 26. Chromium (VI) adsorption-pH curves for montmorillonite at 25° C. Initial Cr(VI) concentrations (ppm) are indicated beside each curve, and the equivalence volume for each curve is 16.7 ml/g montmorillonite.

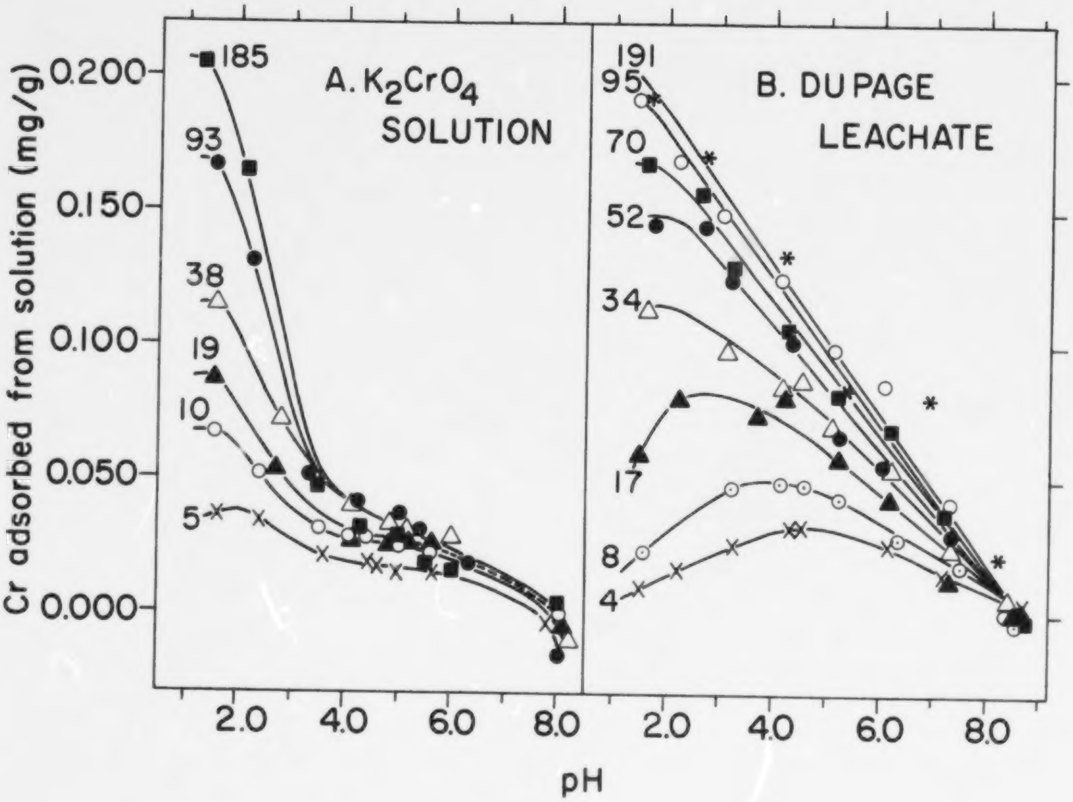

Figure 27. Chromium (VI) adsorption-pH curves for kaolinite at 25° C. Initial Cr(VI) concentrations (ppm) are indicated beside each curve and the equivalence volume for each curve is 10.0 ml/g kaolinite.

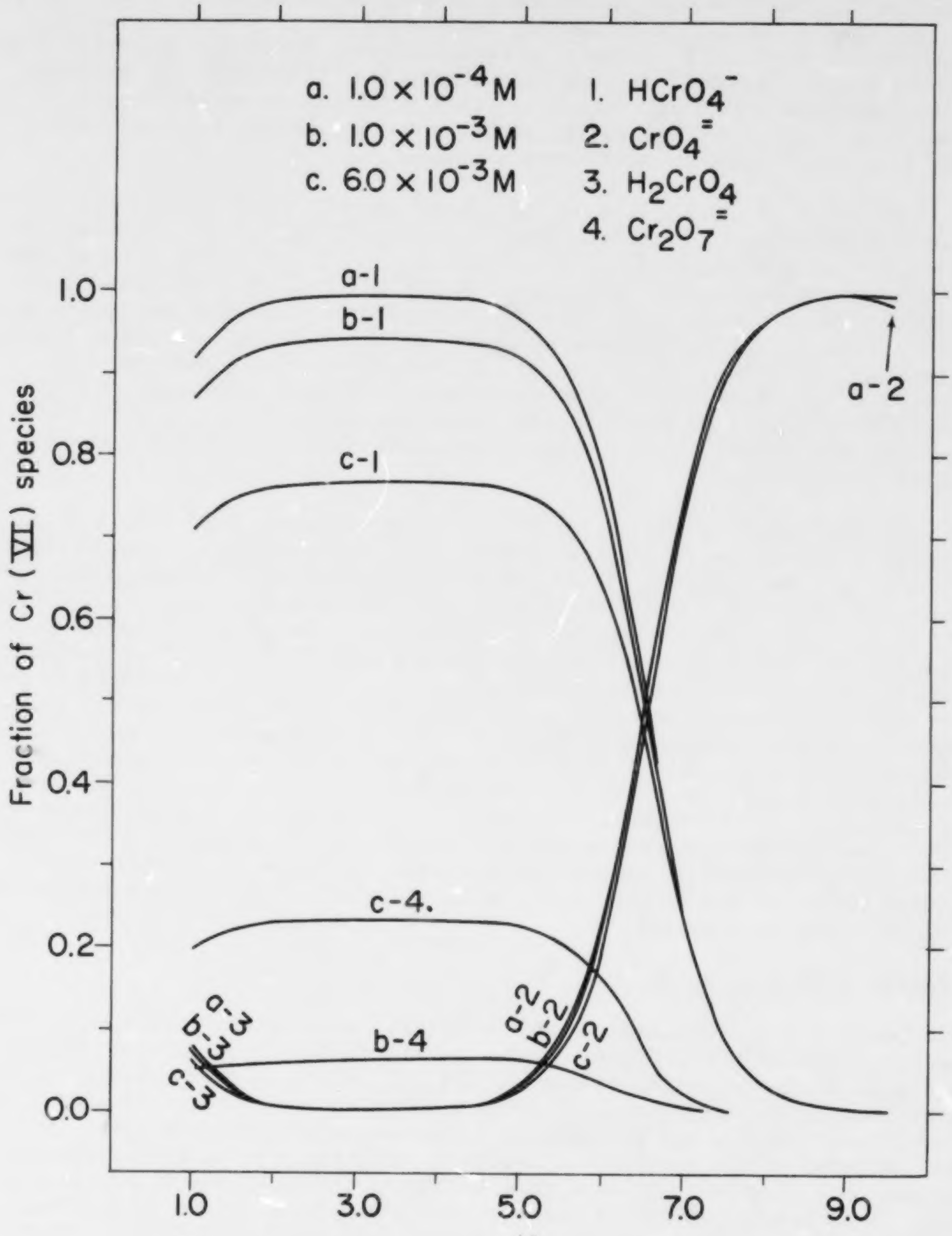

Figure 28. Distribution of Cr(VI) species for various Cr(VI) concentrations.

curves in Figures 26 and 27 using Equation {16} at pH values 3.0, 4.0, 5.0, and 7.0. Sample adsorption isotherms, constructed at pH 4.0, are shown in Figure 29. For both clay minerals, more Cr(VI) was adsorbed from DuPage leachate solutions than from pure K_2CrO_4 solutions throughout the pH range 3.0 to 7.0. This result is contrary to that which was expected. Evidently, anions (e.g., Cl^- and HCO_3^-) in the leachate do not compete favorably with $HCrO_4^-$ ions, or adsorption would have decreased.

The effect of the Cl^- ion on the adsorption of Cr(VI) by clay was determined by adsorption experiments carried out with 20 ppm Cr(VI) in deionized water with and without 1000 ppm of Cl^- added as NaCl. No appreciable change in the adsorption of Cr(VI) was caused by the Cl^- ion. That more Cr(VI) was adsorbed from DuPage leachate than from pure K_2CrO_4 solutions may be the result of formation of polynuclear complexes in the leachate solutions, organic or inorganic in nature, which can be adsorbed by the clay. The high ionic strength of the leachate may also contribute to higher adsorption of Cr(VI) species by a depression of the diffuse double-layer surrounding the clay particles (van Olphen, 1963), which allows more ions to approach the clay surface and be adsorbed.

The adsorption isotherms for Cr(VI) at pH values of 3.0, 4.0, 5.0, and 7.0 were plotted according to the linear form of the Langmuir equation (Equation 16). All the Langmuir plots gave linear regression r^2 values 0.99. The Langmuir plots at pH 4.0 are shown in Figure 30. From the slopes of the Langmuir plots, adsorption maxima were calculated and are presented in Table 12. The difference in the calculated adsorption maxima of montmorillonite and kaolinite reflects the difference in the probable number of available adsorption sites, based on comparison of the structural differences and the surface areas of the two clay minerals (Table 1). The precise mechanism for anion adsorption by clay minerals is uncertain, but we assume, as have others, that anion exchange plays an important role in the adsorption process. However, the adsorption maxima presented in Table 12 represent the maximum amount of Cr(VI) ions adsorbed at some sufficiently high concentration of Cr(VI) ions in solution, whereas the adsorption isotherms in Figure 29 represent the maximum amount of Cr(VI) ions that can be adsorbed at any given concentration of Cr(VI) ions in solution.

Chromium (III) Adsorption

During preliminary experiments on Cr(III) adsorption by kaolinite, the removal curves shown in Figure 31 were obtained. The curve labeled "blank" in Figure 31, representing removal of Cr(III) from a solution containing no clay, shows that precipitation becomes a very important mechanism of Cr(III) removal near pH 5.0. The precipitate formed was blue-gray, and X-ray diffraction patterns of the precipitate showed no definite crystalline structure. Because only HNO_3 and NaOH were used to adjust the pH of the $Cr(NO_3)_3$ solution, it is reasonable to believe that the precipitate formed is a chromic hydroxide. Murray (1956) stated that chromic hydroxide is a hydrous oxide ($Cr_2O_3 \cdot nH_2O$) of indefinite composition that is blue-gray when its water content is high. It was therefore concluded that chromic hydroxide was the precipitate of our experiments.

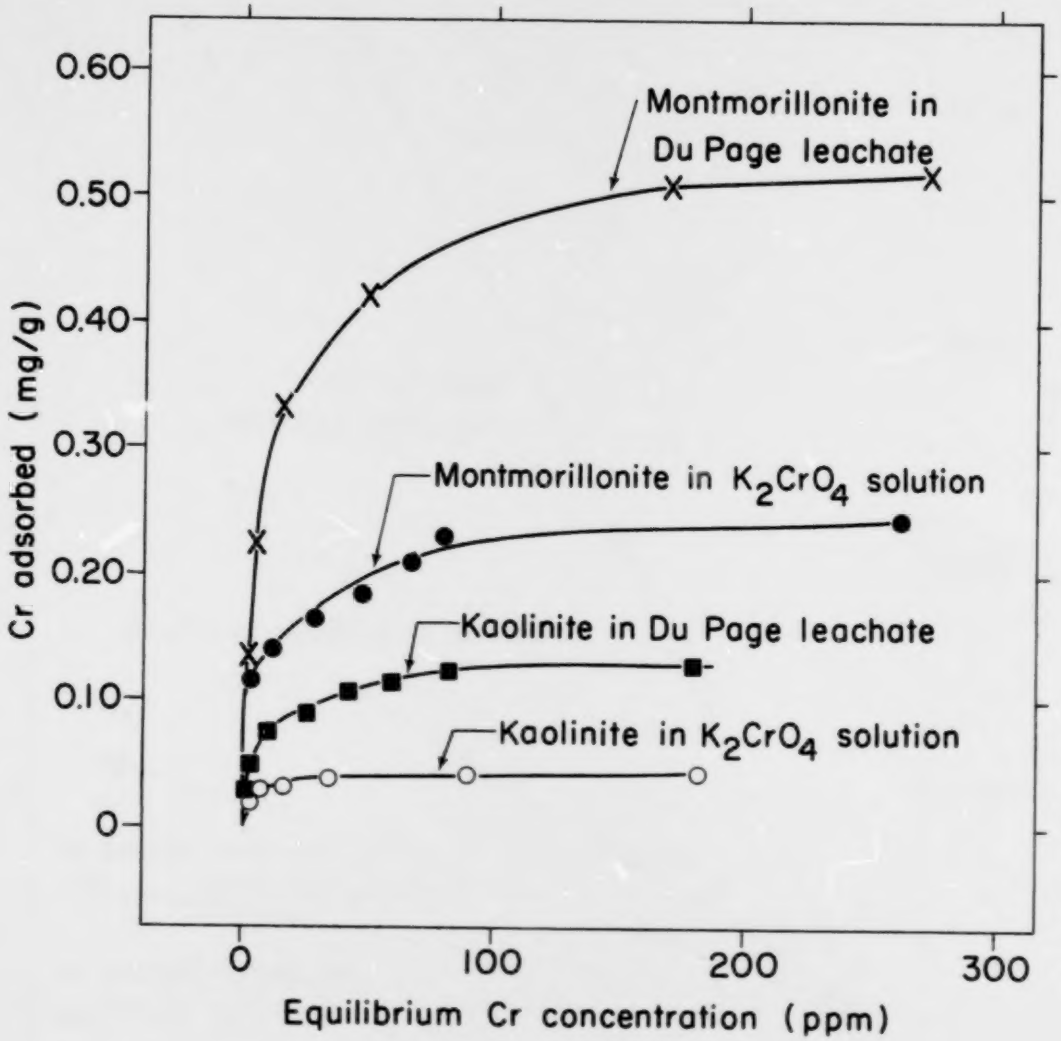

Figure 29. Adsorption isotherms for Cr(VI) at pH 4.0 and 25° C.

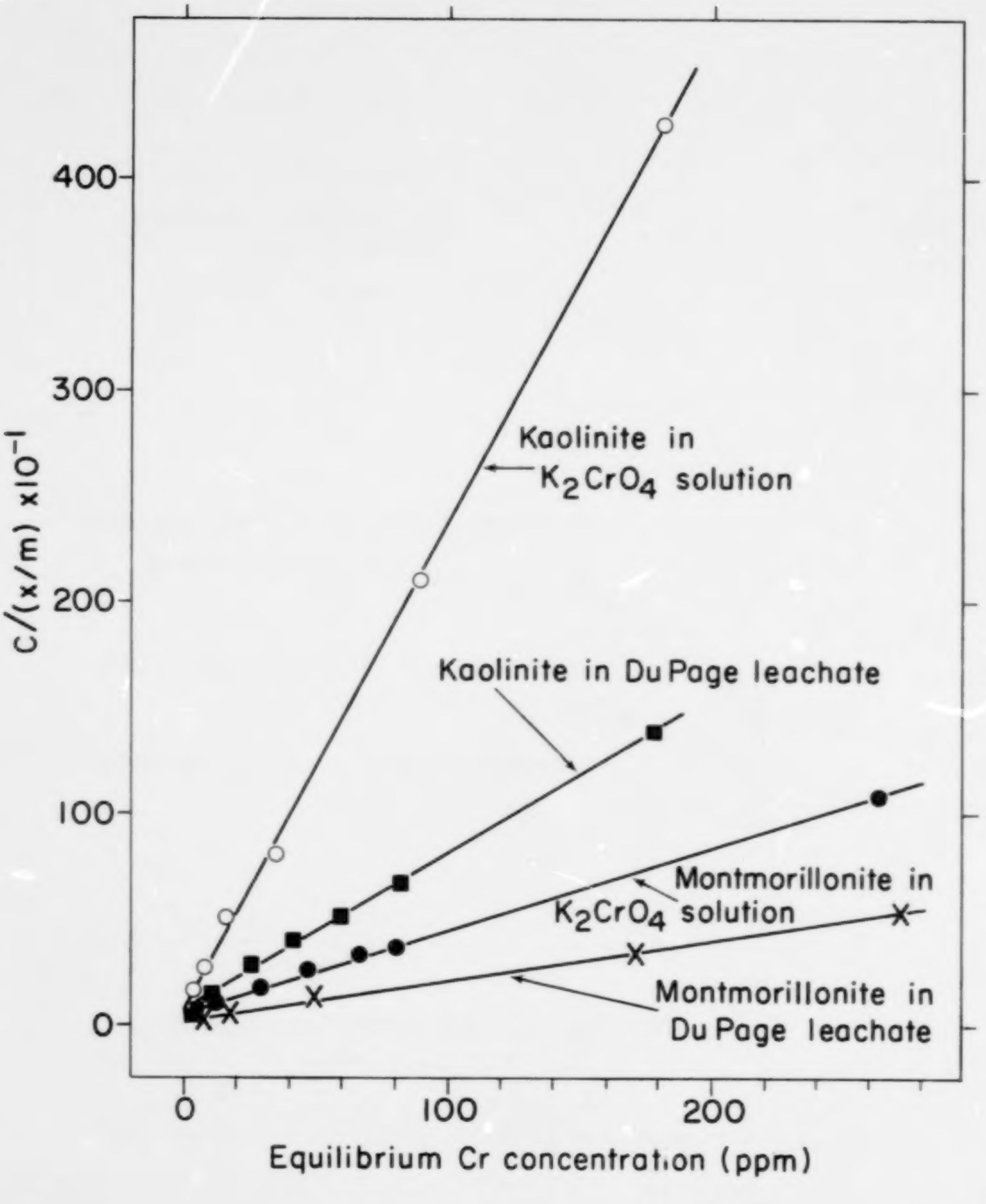

Figure 30. Langmuir plots of Cr(VI) adsorption data at pH 4.0 and 25° C.

TABLE 12. ADSORPTION MAXIMA FOR Cr(VI) BY MONTMORILLONITE AND KAOLINITE AT 25° C FOR VARIOUS pH VALUES

pH	mg/g Pure Solution	 DuPage Leachate Solution
	Montmorillonite	
3.0	0.400	0.667
4.0	0.256	0.526
5.0	0.147	0.417
7.0	0.052	0.169
	Kaolinite	
3.0	0.093	0.189
4.0	0.044	0.130
5.0	0.032	0.115
7.0	0.015	0.051

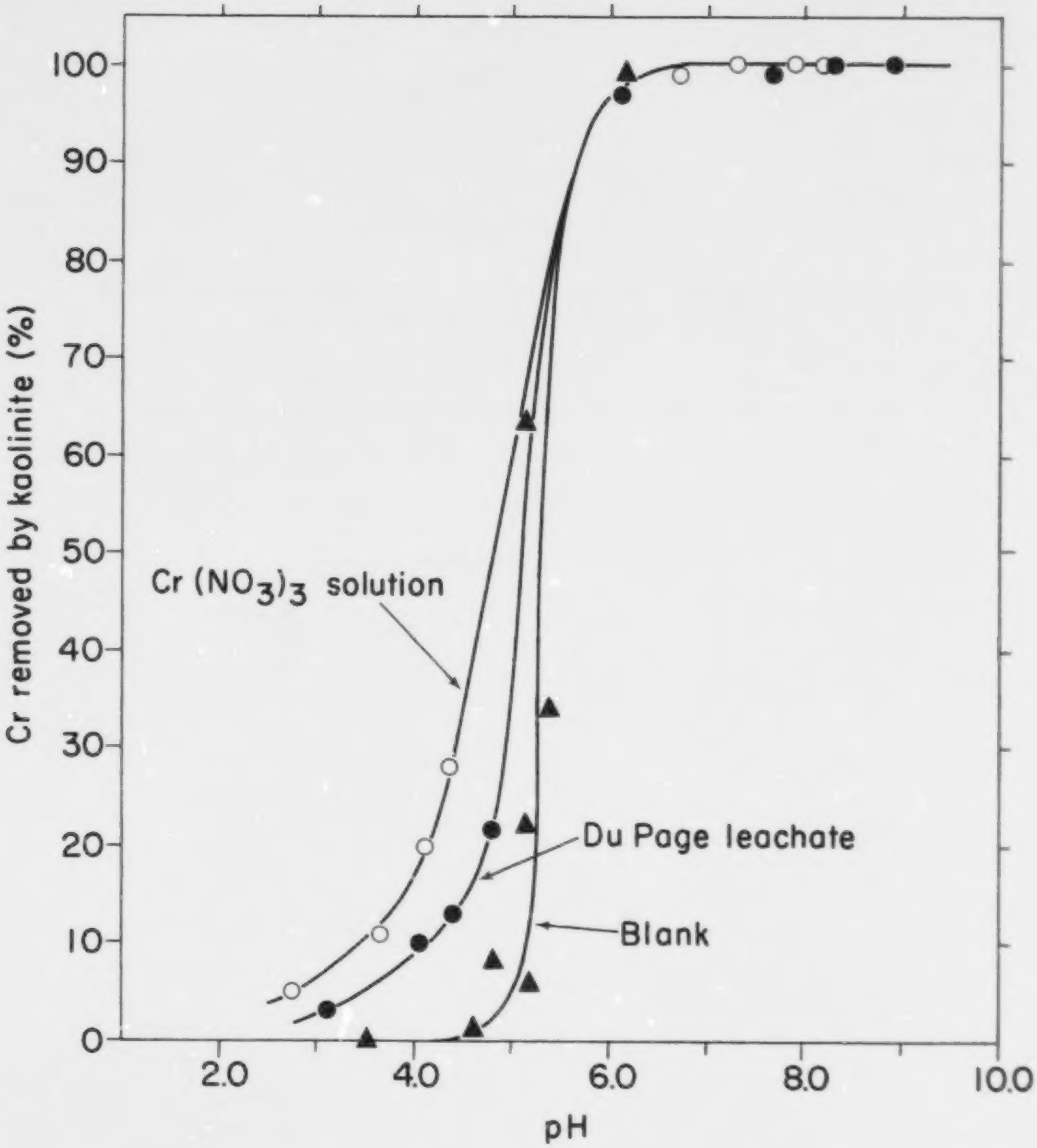

Figure 31. Removal of Cr(III) from solution by kaolinite. The curve labeled "Blank" represents $Cr(NO_3)_3$ solution without kaolinite.

Families of Cr(III) adsorption-pH curves for the pH range 1.5 to 4.5 are presented in Figure 32. Cation exchange is generally accepted as the principal mechanism for cation adsorption by soils and clay minerals. Chromium (III) is known (Rollinson, 1956) to be extensively hydrolyzed in acid solutions to species such as $Cr(OH)^{2+}$, $Cr(OH)_2^{1+}$ or $Cr_2(OH)_4^{2+}$ or $Cr_2(OH_{12})^{6+}$, and $Cr_6(OH)_{15}^{3+}$. Therefore, the increasing adsorption of Cr(III) as pH increases can, in part, be attributed to exchange-adsorption of hydrolyzed Cr(III) species other than Cr^{3+} ions.

Adsorption isotherms were constructed from the adsorption-pH curves (Fig. 32) by using Equation {15} at pH values 2.5, 3.0, and 4.0. The isotherms constructed for pH 4.0 are shown in Figure 33. As was expected, the adsorption of Cr(III) by the clay minerals is lower in DuPage leachate than in pure $Cr(NO_3)_3$ solutions. However, significantly less reduction in adsorption of Cr(III) from DuPage leachate (3% to 14%) took place than observed in tests of Pb, Cu, Zn, and Cd adsorption from DuPage leachate by the same clay minerals. The Cr(III) species existing in solution are so strongly adsorbed that the cations present in the DuPage leachate do not effectively compete with the Cr(III) species for exchange-adsorption sites.

The adsorption isotherm data for Cr(III) at pH values 2.5, 3.0, and 4.0 were plotted according to the Langmuir equation (Equation {16}) and the Langmuir plots for the pH 4.0 adsorption isotherms are shown in Figure 34. Adsorption maxima calculated from the slopes of the Langmuir plots in Figure 34 are presented in Table 13. The amounts of the various hydrolyzed Cr(III) species that could be adsorbed via a cation exchange mechanism by the montmorillonite and kaolinite clay minerals that had CEC values of 79.5 meq/100 g and 15.1 meq/100 g, respectively, are presented in Table 13, because, if cation exchange is the principal adsorption mechanism, the ratio of the adsorption maxima should be about equal to the ratio of the CEC values for the two clay minerals.

At pH 2.5 the adsorption maximum ratio is close to the CEC ratio (Table 13), but the adsorption maxima themselves are higher than those based on exchange adsorption of Cr^{3+} ions. This implies that some hydrolyzed Cr(III) species are being adsorbed even at pH 2.5. The question arises, however, as to the validity of using CEC values obtained from NH_4^+ ion exchange at pH 7.0 to calculate the expected adsorption maxima at pH 2.5. However, as there is a general relative correlation between the adsorption maxima and CEC values, it is reasonable to use adsorption maxima calculated from CEC values for comparison purposes. At pH 4.0, the ratio of the adsorption maxima increases to about 13, and the amount of Cr(III) adsorbed by montmorillonite is even larger than would be expected from the exchange adsorption of the $Cr_6(OH)_{15}^{3+}$ ion.

The high adsorption maximum ratio at pH 4.0 is the result of the large adsorption maximum obtained for montmorillonite, which appears to be indirectly caused by our experimental procedure. The rates of some of the Cr(III) hydrolysis reactions are very slow, and, in one reported case (Laswick and Plane, 1959), about 107 days were required for Cr(III) solutions, even at elevated temperatures, to reach equilibrium. In our Cr(III) experiments, the clay mineral suspensions were adjusted to a particular pH value,

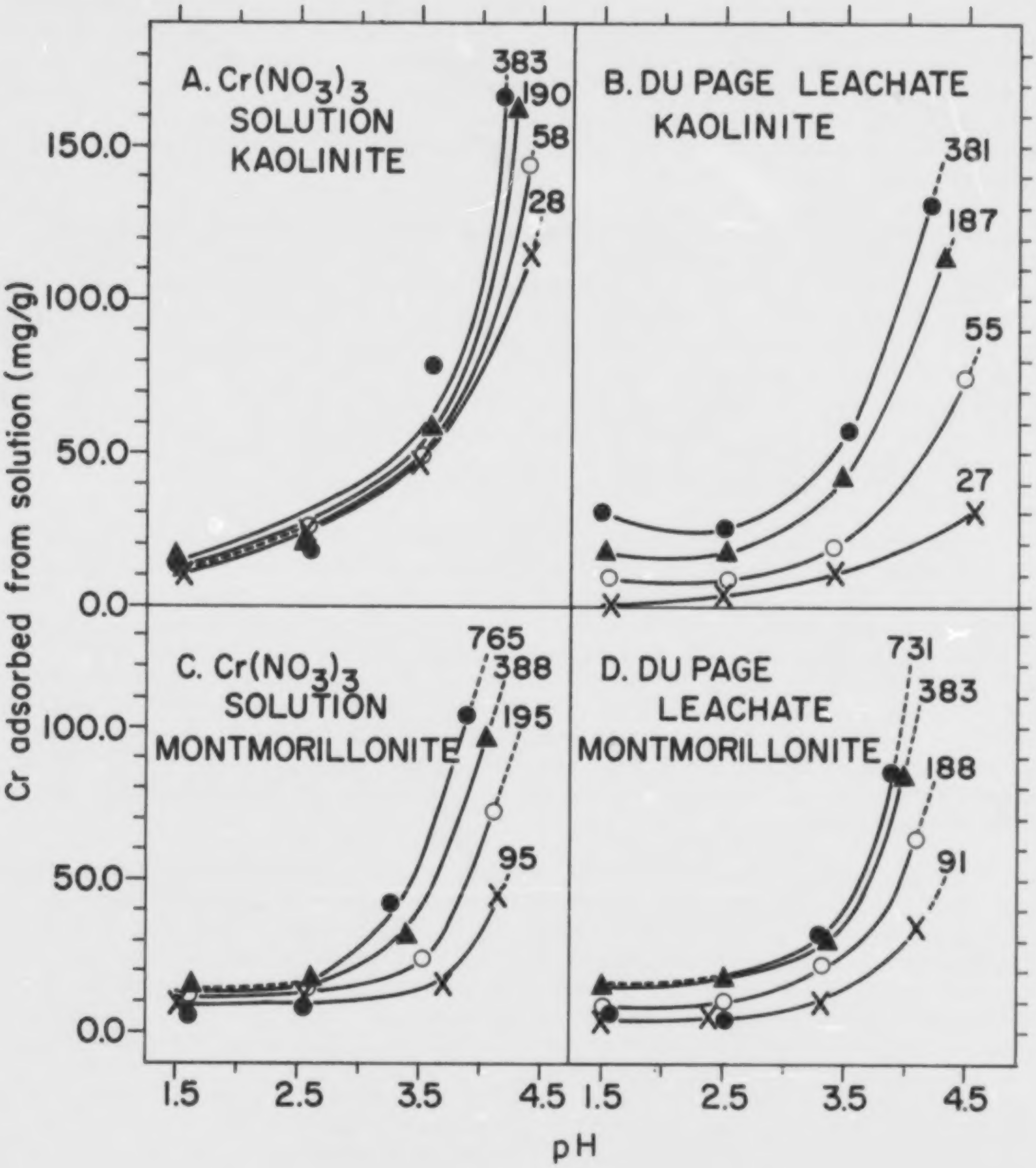

Figure 32. Chromium (III) adsorption-pH curves at 25° C. Initial Cr(III) concentrations (ppm) are indicated beside each removal curve, and the equivalence volume for each curve is 500.0 ml/g kaolinite.

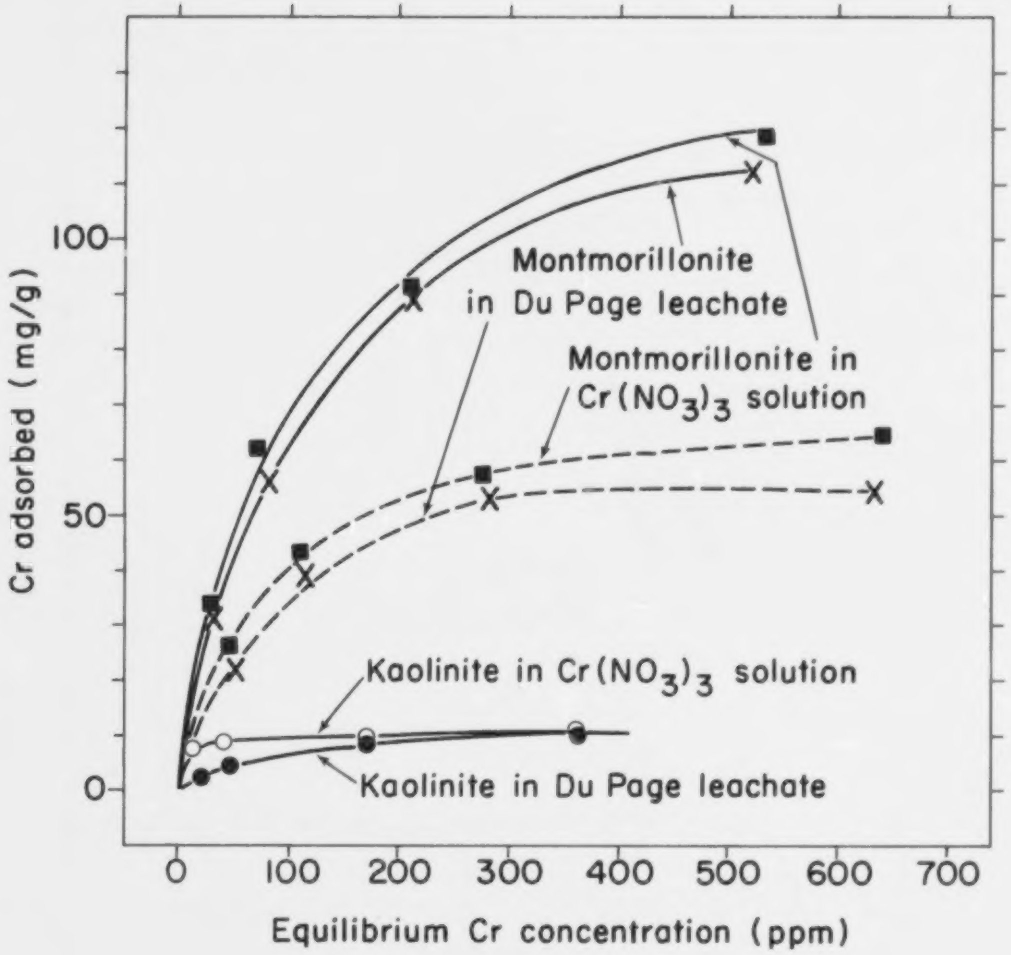

Figure 33. Chromium (III) adsorption isotherms at pH 4.0 and 25° C. The plots shown in dotted lines were obtained from the "corrected" adsorption-pH curves.

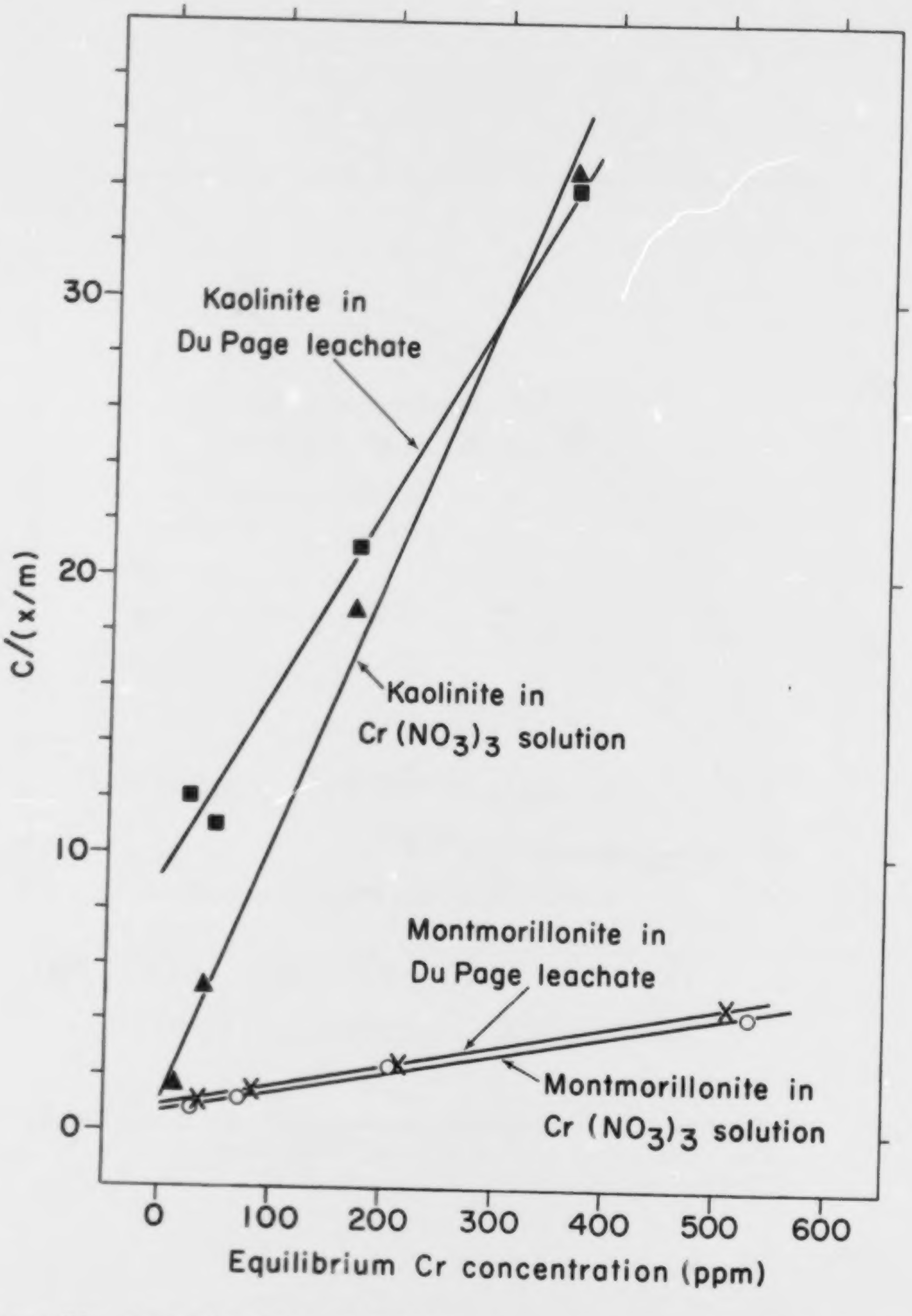

Figure 34. Langmuir plots of Cr(III) adsorption data at pH 4.0 and 25° C.

TABLE 13. ADSORPTION MAXIMA FOR Cr(III) BY MONTMORILLONITE AND KAOLINITE AT 25° C FOR VARIOUS pH VALUES

(mg/g)									
pH 2.5		pH 3.0		pH 4.0		Values Based on CEC for Different Species			
P[a]	L[b]	P	L	P	L	Cr^{+3}	$Cr(OH)^{2+}$	$Cr(OH)_2^+$	$Cr_6(OH)_{15}^{3+}$
Montmorillonite									
17.9	--	33.7	32.8	139.6	136.1	13.8	20.7	41.4	82.7
Kaolinite									
3.3	--	5.0	5.0	10.7	14.7	2.6	3.9	7.8	15.6
Ratio of Adsorption Maxima									
5.4	--	6.5	6.6	13.0	9.3	5.3	5.3	5.3	5.3

[a] Pure solutions, [b] DuPage leachate solutions

such as 4.5. After a few hours, hydrolysis caused the pH of the suspensions to drop. The pH of the suspensions were readjusted to 4.5, but the pH again dropped because of hydrolysis. The pH of the suspensions were all readjusted to the desired pH value several times during a period of two weeks. They were then shaken for 2 days before a final pH value was measured, and the suspensions were centrifuged. What appears to occur in the pH range 3.5 to 4.5 is as follows. Adsorption plus possible precipitation of Cr(III) takes place at the higher initial pH values to which the suspensions had been adjusted. But, when the pH of the suspensions drops due to hydrolysis, desorption of Cr(III) species from the clay mineral or dissolution of any precipitate formed apparently does not occur at rates fast enough to achieve true equilibrium in the clay suspension. The pH values of the montmorillonite suspensions showed larger decreases in pH than the kaolinite suspensions; this apparently produces much larger differences between the calculated and true equilibrium adsorption maxima for montmorillonite than for kaolinite.

The adsorption-pH curves shown in Figure 32 were replotted as the amount of Cr(III) adsorbed versus the highest pH values to which the clay suspensions were adjusted. The adsorption isotherms were calculated from the "corrected" adsorption-pH curves at pH 4.0 and are shown as the dotted isotherms for montmorillonite in Figure 33. The "corrected" adsorption isotherms for kaolinite are almost superimposable on the isotherms shown in Figure 33, and, therefore, were omitted. Adsorption maxima from pure $Cr(NO_3)_3$ solutions, calculated by Langmuir plots of the "corrected" isotherms at pH 4.0, are 72.2 mg/g for kaolinite. Thus, the "corrected" adsorption maxima agree with an exchange-adsorption mechanism involving hydrolyzed Cr(III) species. We have learned, as Laswick and Plane (1959) pointed out, that the changes that Cr(III) species undergo are generally quite slow, which makes the interpretation of the experiments difficult.

CONCLUSIONS

The results of this study indicated that Cr(III) yielded the strongest attenuation of all the heavy metals studied. This suggests that landfill disposal of Cr(III) wastes would exhibit low mobility and probably would initiate fewer pollution problems than would the other heavy metals. Above pH 6, Cr(III) should be immobile because of precipitation. Below pH 4, Cr(III) species were strongly adsorbed by both kaolinite and montmorillonite and would have a relatively low mobility through soils or clay minerals used as landfill liners. Between pH 4 and 6, the combination of adsorption and precipitation should render Cr(III) quite immobile.

In the pH range 1.5 to 4.0, 30 to 300 times more Cr(III) than Cr(VI) was adsorbed by the clay minerals; and at higher pH values the ratio (Cr(III) removed)/(Cr(IV) removed) became even larger because of increased Cr(III) removal and decreasing adsorption of Cr(VI). The adsorption of Cr(VI) was low relative to Cr(III), even at very low pH values where Cr(VI) adsorption was strongest. Cr(VI) adsorption was the weakest of the heavy metals studied and was markedly reduced as the pH was raised into the alkaline range. Thus, it would become very mobile at high pH. Since Cr(VI) is the most toxic and mobile form of Cr, landfill disposal of Cr(VI) wastes can potentially cause serious pollution problems even if the landfill has a thick clay liner. The results of this study suggest that a conversion of Cr(VI) wastes to Cr(III) by a process such as that devised by Shiga (1975) would greatly reduce the hazard to water resources from Cr(VI) wastes disposed of in landfills.

SECTION 10

EFFECT OF pH ON ADSORPTION OF As AND Se FROM LANDFILL-LEACHATE BY CLAY MINERALS[1]

ABSTRACT

The effect of pH and ionic competition on arsenate (As(V)), arsenite (As(III)), and selenite (Se(IV)) adsorption by kaolinite and montmorillonite clay minerals from municipal landfill-leachate solutions were determined.

The results showed that pH had a strong influence on the amounts adsorbed of all three of the elemental forms studied. Montmorillonite clay was found to adsorb about twice as much As or Se as kaolinite. Leachate was found to have little effect on the adsorption of As(V) or Se(IV), while As(III) adsorption was reduced 30 to 50%. It was concluded that the principal adsorption mechanism was anion exchange of the monovalent species of each elemental form.

The results of the study suggest that land disposal of As and Se wastes under alkaline conditions represents a potentially high pollution hazard.

INTRODUCTION

As and Se are quite toxic (U.S.-EPA, 1972) and, therefore, they have a high potential to produce pollution problems. The U. S. Environmental Protection Agency (EPA) cites several examples of instances where land disposal of arsenic wastes have resulted in the poisoning of drinking water wells (U.S.-EPA, 1973) and selenium has been reported to have polluted ground water as far as two miles from a dump on Long Island (Garland and Mosher, 1975). As and Se waste streams may be liquids, suspensions, or sludges. Sample waste streams from copper, lead, and zinc smelting, from duplicating and photo equipment manufacturing, and from pharmaceutical industries have been measured and reported to contain from 1,000 to 30,000 ppm As and from 3,000 to 50,000 ppm Se (Lehman, 1973). These waste streams may be disposed of on land in lagoons, in landfills, or by spreading. Land spreading of municipal wastewater effluents (U.S.-EPA, 1975) and sewage sludges which may contain low concentrations of As and Se is now being considered as a viable alternative to treatment.

The purpose of this study was to provide some basic data regarding the effect of pH on the removal of As and Se from landfill-leachate by kaolinite and montmorillonite, which are common clay minerals found in soils. The results of the present study give insights into whether or not As and Se waste streams can be safely disposed of in properly designed landfills for municipal solid waste. The results of the study also provide basic information on the mobilities of As and Se through soils. This can be of aid in the design of land disposal systems for As and Se waste streams in general.

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[1] Authors: R. R. Frost and R. A. Griffin

EXPERIMENTAL

Appropriate stock solutions of As(V) and As(III) were prepared by dissolving reagent grade Na_2HAsO_4 or $NaAsO_2$ in deionized water. Se(IV) stock solutions were prepared by dissolving pure selenium metal in a minimum amount of 1:1 HNO_3. Some heating of the solution was necessary to speed up the dissolution. All stock solutions were adjusted to about pH 5 before use.

Fifty ml aliquots of leachate were pipeted into 125-ml Erlenmeyer flasks containing from 1.00 to 5.00 g of either kaolinite or montmorillonite. The weight of clay used was chosen so that the amount of arsenate, arsenite, or selenite removed from the leachate solutions could be determined with some precision from the difference between the initial and final solution concentrations. Several replicates of each clay suspension were prepared. The pH values of the replicate clay suspensions were adjusted with HNO_3 or NaOH to different values over the pH range 1 to 9. The clay suspensions were shaken overnight and then 2.0 ml of an appropriate pH 5 stock solution of either As or Se was pipeted into the flasks. Of the several experimental procedures possible, the procedure used gave the most satisfactory results. The As or Se clay suspensions were then shaken in a constant temperature bath at 25 ± 0.5^{o} C for at least 24 hours to insure complete equilibration. The equilibrium pH values of the clay suspensions were measured, the clay suspensions centrifuged, and the supernatant solutions analyzed for their As or Se concentration by atomic adsorption spectroscopy. A $NO\text{-}C_2H_2$ flame was used for As analyses, and air-C_2H_2 flame was used for Se analyses. Blanks (i.e., no clay) were prepared along with the clay suspensions and were also analyzed to determine the initial As or Se concentration. The amount of As or Se removed from solution by a given clay at a particular pH was determined as:

$$\text{(initial - equilibrium conc.)} \times \frac{\text{total sol'n vol. after pH adjustments}}{\text{sample weight.}} \qquad \{17\}$$

The amount of As or Se removed from solution was then plotted as a function of pH. From the initial concentration of As or Se in solution, the weight of clay used, the final solution volume after pH adjustments, and the removal versus pH curves themselves, "adsorption" or "removal" isotherms can be constructed at different pH values by use of the following equation:

$$\text{Equilibrium C (ppm)} = \text{Initial C (ppm)} - \frac{\text{Am't. removed } (\mu g/g) \times \text{Wt. Clay (g)}}{\text{Final solution volume (ml)}}. \qquad \{18\}$$

RESULTS AND DISCUSSION

Arsenate (As(V)) and Arsenite (As(III)) Adsorption

Curves for the removal of As(V) from leachate by kaolinite and montmorillonite versus pH are shown in Figure 35. It is interesting to note that the amount of As(V) removed from solution goes through a maximum at about pH 5. The distribution of arsenate species in solution as a function of pH is shown in Figure 36a. Comparison of Figure 35 with Figure 36a shows that the As(V) removal curves follow the monovalent $H_2AsO_4^-$ species curve reasonably well. Thus, it was concluded that the $H_2AsO_4^-$ ion is the principal As(V) ion being adsorbed by the clay minerals. The non-adsorption or depressed adsorption of the $HAsO_4^=$ ion is apparently due to the occurrence of negative charges on adjacent oxygen atoms in the tetrahedral $HAsO_4^=$ ion which results in repulsion of the ion from the clay surface. Some As(V) precipitation was observed to occur above approximately pH 9 and can be seen on the removal curves in Figure 35 as the curves turn upward around pH 9.

Curves for the removal of As(III) from leachate by kaolinite and montmorillonite versus pH are shown in Figure 37. In general, an increase in adsorption of As(III) is observed as pH increases in the range 3 to 9. The montmorillonite removal curves in Figure 37 show an interesting peak about pH 7. There is some question as to what As(III) species are present in the leachate solutions and which As(III) species is actually being adsorbed. From a study of As(III) adsorption by an anion exchange resin (Everest and Popiel, 1957), the $As_3O_5^-$ on $As_3(OH)_{10}^-$ species was proposed as the species being adsorbed in the pH range 5 to 6, but the fraction of the total As(III) in solution existing as the $As_3O_5^-$ ($As_3(OH)_{10}^-$) species is small and the amount of exchange adsorption was low. Other As(III) species apparently existing in solution are $As_2O_4^=$ ($As_2(OH)_8^=$), $As(OH)_3$, $As(OH)_4^-$, and $AsO_2OH^=$ -- with the latter two species becoming important above pH 9. Whatever As(III) species are present in solution, the fraction of the total As(III) in solution present as monovalent As(III) species will increase as pH increases. Thus, the amount of As(III) adsorption should increase as pH increases as observed in Figure 37. There is no apparent explanation for the observed peaks about pH 7 on the montmorillonite removal curves in Figure 37. Although no peaks are observed on the kaolinite removal curves in Figure 37, they might have appeared if more data points were obtained in the pH range 6.5 to 7.

Comparison of removal curves (not shown) for As(V) and As(III) from deionized water solutions obtained at a single concentration for each clay mineral with the corresponding leachate removal curves showed that the anion competition present in the leachate surpresses the adsorption by the clay minerals of As(V) slightly and of As(III) by some 30 to 50 percent.

Isotherms calculated from the removal curves in Figures 35 and 37 at pH 5.0 are shown in Figure 38. The higher adsorption of As(V) and As(III) by montmorillonite compared to kaolinite simply reflect the structural and surface area differences between the two clay minerals. Anion exchange sites are thought to exist primarily at the broken edges of clay minerals (Grim, 1968).

Montmorillonite clay was found to adsorb approximately twice as much As as kaolinite. Examination of the surface area data, as measured by N_2 gas adsorption given in Table 1, suggests that the montmorillonite has roughly twice as much edge surface area as the kaolinite. The tetrahedral $H_2AsO_4^-$ ion can align itself with the silica tetrahedral of the clay lattice and can form

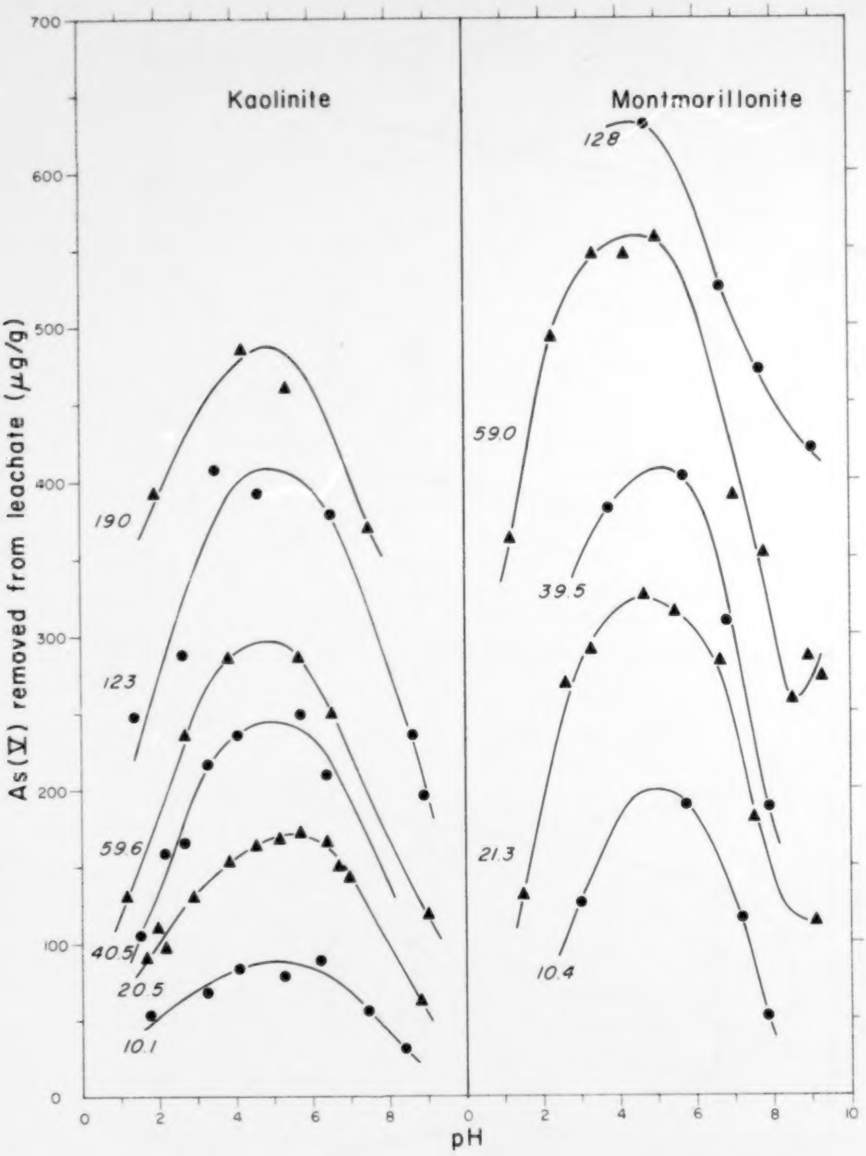

Figure 35. The amount of As(V) removed from DuPage leachate solutions by kaolinite and montmorillonite at 25° C plotted as a function of pH. Labels are the initial solution concentration of As(V) in ppm. Each datum point was obtained by using either 4 g of kaolinite of 1 g of montmorillonite in a total solution volume of 52.2 ml.

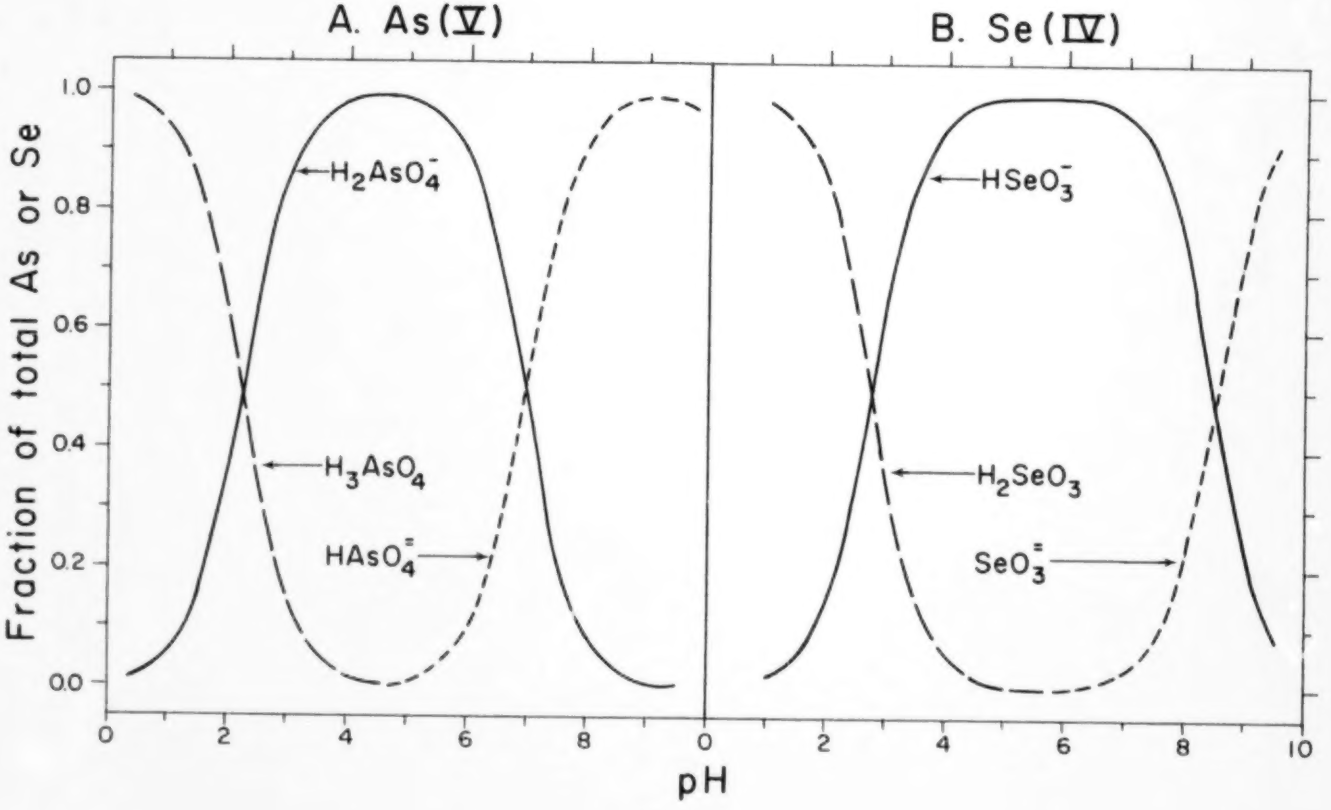

Figure 36. Species distribution diagram for As(V) and Se(IV).

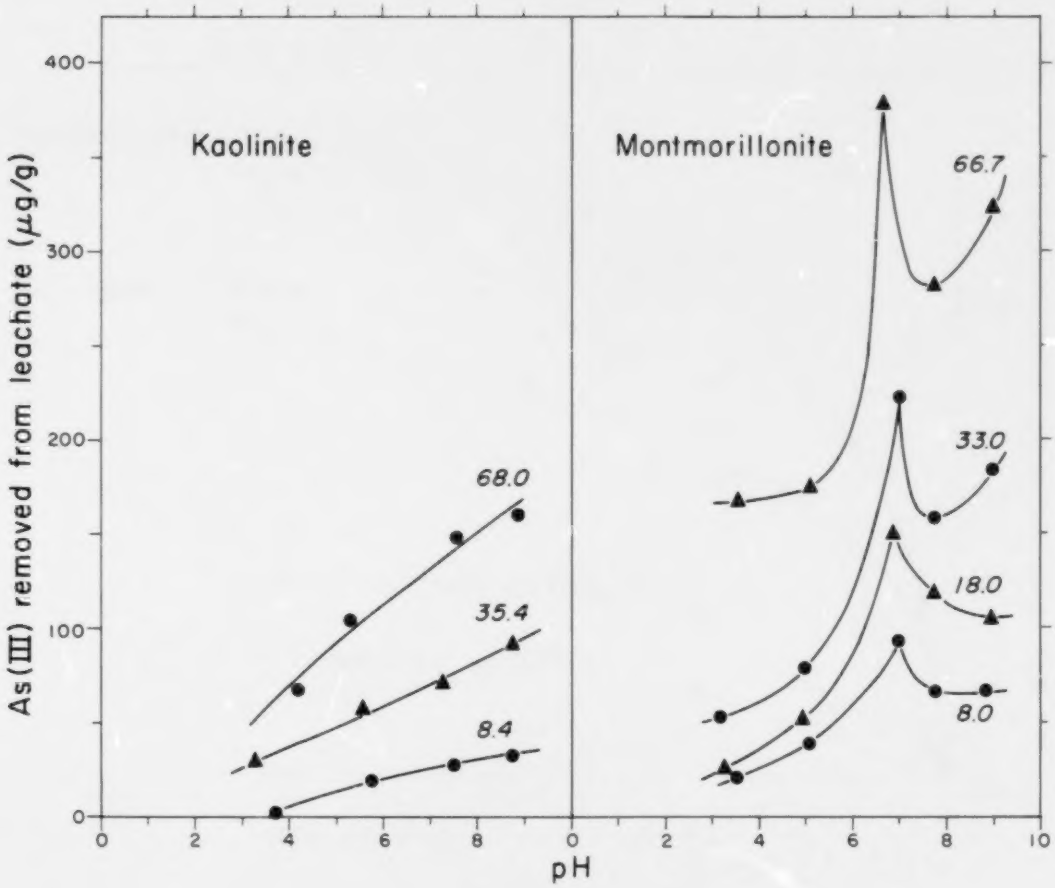

Figure 37. The amount of As(III) removed from DuPage leachate solutions by kaolinite and montmorillonite at 25° C plotted as a function of pH. Labels are the initial solution concentration of As(III) in ppm. Each datum point was obtained by using 4 g of clay in a total solution volume of 52.5 ml.

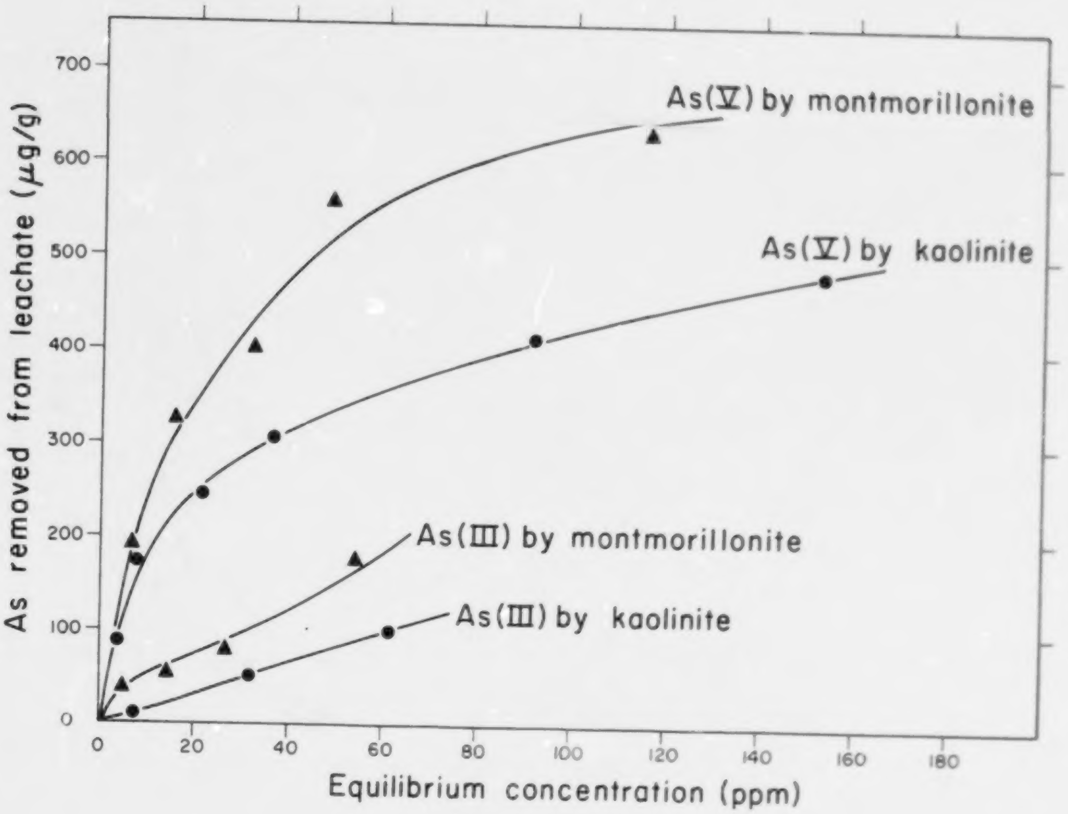

Figure 38. The amount of As(V) or As(III) removed from DuPage leachate solutions at pH 5.0 and 25° C per gram of clay plotted as a function of the equilibrium arsenic concentration.

an extension of the crystal lattice which has a relatively high bond strength. The arsenate ion can be compared to the large $As_3(OH)_{10}^-$ ion which is not tetrahedral and thus is unable to align itself as effectively on the clay edges. It was therefore concluded that the principal adsorption mechanism was anion exchange of the monovalent species of each elemental form.

Selenite (Se(IV)) Adsorption

Curves for the removal of Se(IV) from leachate by kaolinite and montmorillonite versus pH are shown in Figure 39. The removal of Se(IV) goes through a maximum in the pH range 2 to 3 and then decreases as the pH increases. The distribution of Se(IV) species in solution as a function of pH is shown in the Figure 36b. Although it is not as apparent as for As(V), the monovalent $HSeO_3^-$ ion appears to be the species predominantly adsorbed by the clay minerals. It is evident from the data in Figure 39 that the adsorption of Se from solution is rapidly converging on zero removal at approximately pH 10, which is the value at which the $HSeO_3^-$ species disappears from solution.

This is evidenced by examining the species distribution diagram presented in Figure 36b. The $HSeO_3^-$ ion has a trigonal-pyramidal configuration which may account for its reduced adsorption; by contrast, the $H_2AsO_4^-$ ion has a tetrahedral configuration. Thus, the configuration of the $HSeO_3^-$ ion must be an inhibiting factor in its adsorption by the clay minerals. On the other hand, pH must play a significant role in modifying the clay mineral surface structure so that increasing adsorption occurs with decreasing pH until the point where a significant fraction of the total Se(IV) in solution is present as the H_2SeO_3 specie. At this point, adsorption starts to decline sharply as the pH is lowered below a value of 2.

Comparison of removal curves (not shown) for Se(IV) from deionized water solutions obtained at a single concentration for each clay mineral with the corresponding leachate removal curves showed that the leachate supresses the adsorption of Se(IV) by the clay minerals slightly. This is presumed to be due to competition for anion exchange sites by the high concentrations of anions present in leachate (Table 2) with the $HSeO_3^-$.

Isotherms calculated from the removal curves in Figure 39 at pH values 3.0, 5.0, and 7.0 are shown in Figure 40. The higher adsorption of Se(IV) by montmorillonite compared to kaolinite simply reflects the structural and surface area differences between the two clay minerals as previously discussed.

CONCLUSIONS

The results of this study indicate that pH has a pronounced effect on the amounts of As(V), As(III), and Se(IV) adsorbed from leachate by clay minerals. It was concluded that the principal adsorption mechanism was anion exchange and, from species distribution diagrams, that the adsorption was due principally to the monovalent species of each element studied, thus leading to the strong pH dependency of the adsorption process.

The results of the study suggest that optimum As removal by soil materials from waste streams would be achieved by conversion of any As(III) to

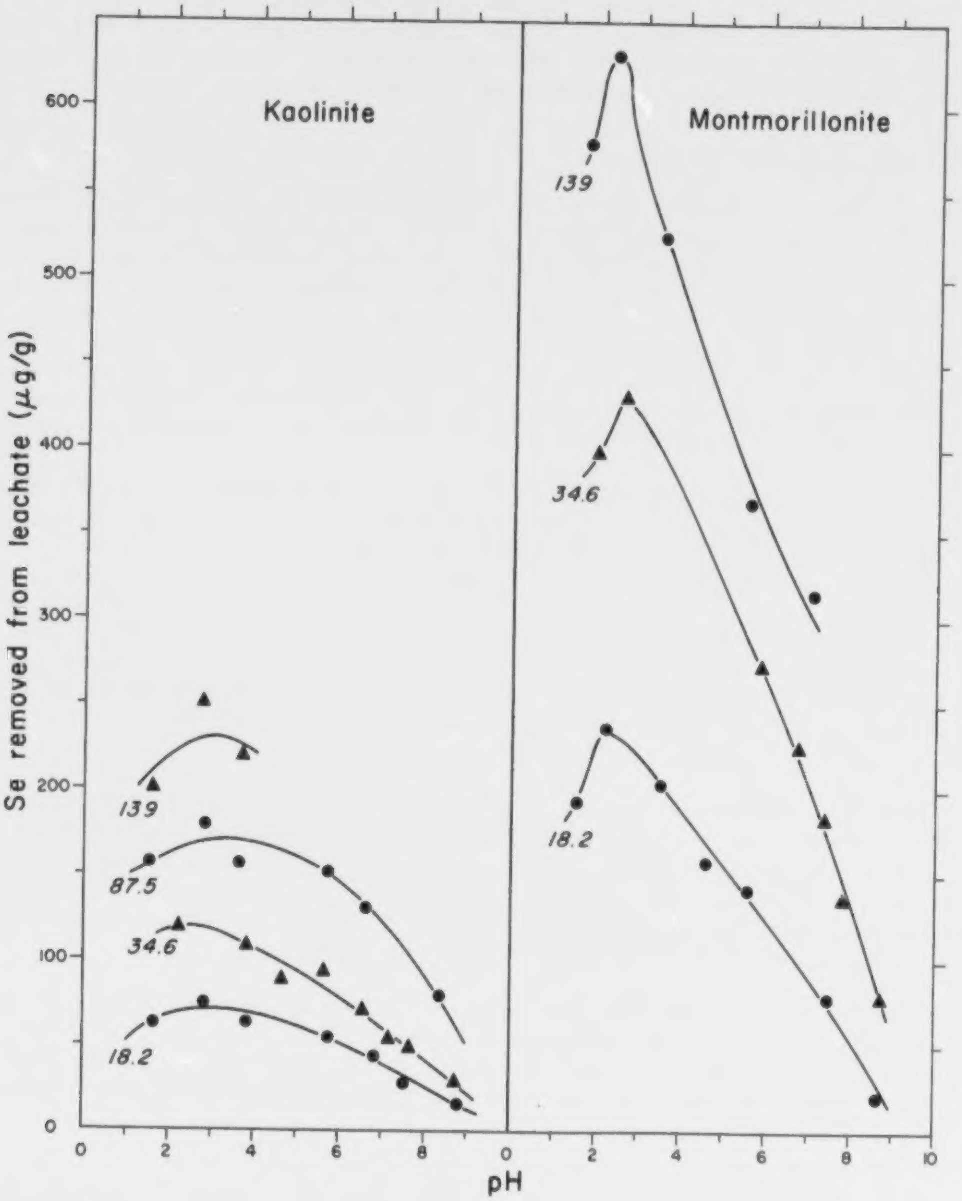

Figure 39. The amount of Se(IV) removed from DuPage leachate solutions by kaolinite and montmorillonite at 25° C plotted as a function of pH. Labels are the initial solution concentration of Se(IV) in ppm. Each datum point was obtained by using either 5 g of kaolinite or 1 g of montmorillonite in a total solution volume of 52.5 ml.

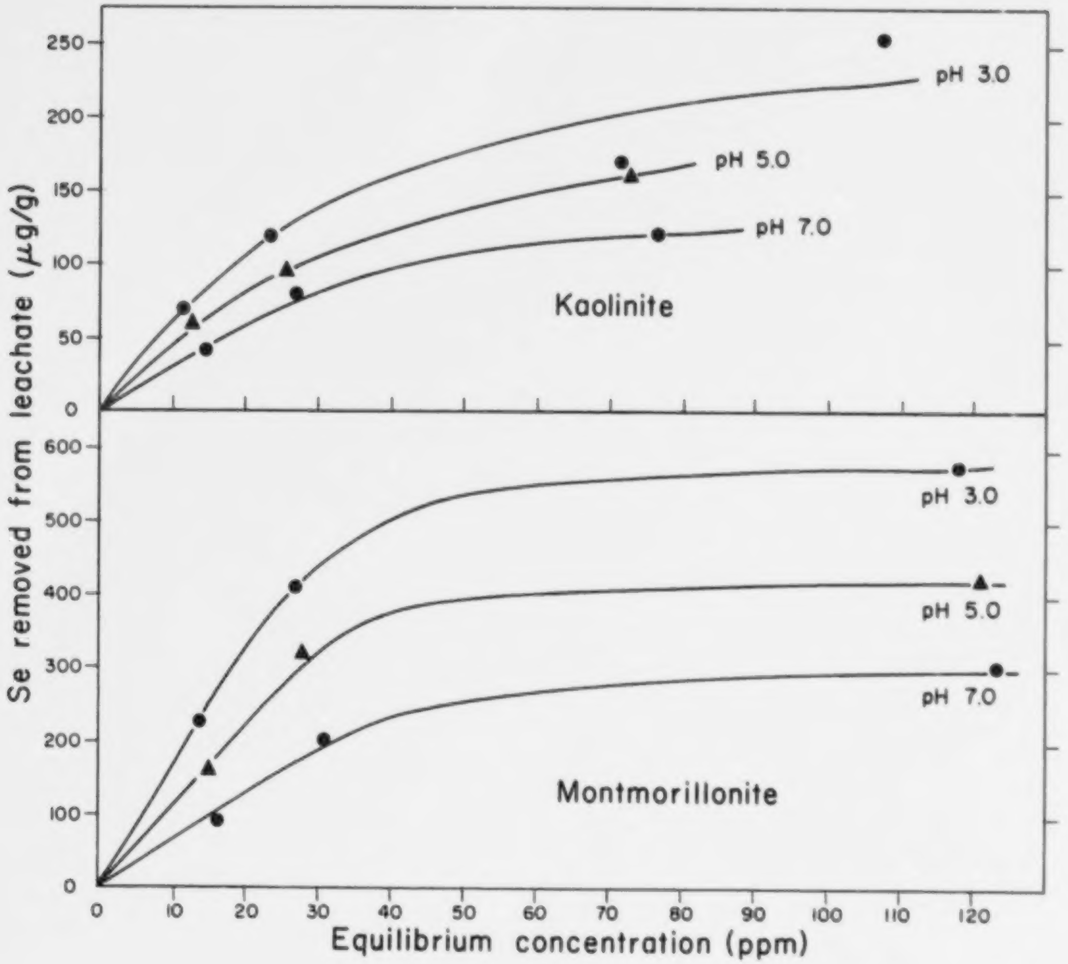

Figure 40. The amount of Se(IV) removed from DuPage leachate solutions at 25° C and several pH values per gram of clay plotted as a function of the equilibrium Se concentration.

As(V), and disposal of the waste in montmorillonitic soils at pH 5. Optimum Se(IV) removal would result from disposal in a montmorillonitic soil at a pH of 2 to 3. A high mobility and hence potential pollution hazard would be expected from land disposal of As(V) or Se(IV) wastes under alkaline conditions.

SECTION 11

MERCURY REMOVAL FROM LEACHATE BY CLAY MINERALS[1]

ABSTRACT

Preliminary investigations regarding the effect of pH on the amounts of Hg removed from DuPage leachate solutions by the two clay minerals, kaolinite and montmorillonite, are reported.

Large amounts of Hg were removed from leachate, both in the presence and absence of clay. This removal of Hg increased as the pH was raised. It was estimated that 70 to 80% of the Hg was removed from leachate by precipitation and/or volatilization, thus indicating that these were the predominant attenuation mechanisms. Removal by clay accounted for 20 to 30% of the observed Hg removal. About two thirds of the Hg removed by the clay was found to be organic-Hg, and about one third was inorganic-Hg.

The results indicated that maximum Hg removal from leachate would be achieved by disposal in montmorillonite clays or soils under alkaline pH conditions.

INTRODUCTION

Because Hg has been the subject of many publications, its occurrence and toxicity will be discussed only briefly here. There are two basic sources of Hg in the environment: as it occurs in nature, and as it is redistributed in nature by man's actions. Hg is widely distributed in the air, soil, and water in low concentrations (Klein, 1972). Man in his utilization of Hg-related technology has at times redistributed this Hg in nature. It is this source of Hg in the environment that we must concern ourselves with since it often results in the release of dangerously high Hg concentrations (Goldwater, 1971).

The main source of environmental Hg contamination has been in the industrial sector (D'Itri, 1972a), and much of this can be attributed to wastewater discharge into rivers and streams (Turney, 1972; Derryberry, 1972). A great deal of the mercurial waste, both organic and inorganic, disposed of in this manner can be directly or indirectly converted by anaerobic microbes into mono- or di-methyl-mercury (D'Itri, 1972a; Greeson, 1970), both of which have been found to be extremely toxic.

As a result of studies on Hg contamination and poisoning, the disposal of industrial mercurial wastes is carefully controlled. However, the potential for contamination still exists where gaps in knowledge preclude enlightened disposal practices. This potential also exists at municipal landfill sites accepting mercurial wastes. The leachates generated from these sites are anaerobic and therefore have the ability to convert mercurial wastes into their toxic forms. Since Hg is incorporated into many industrial or consumer products such as paints, pharmaceuticals, paper products, fluorescent lamps, mercury batteries, etc., the indiscriminate disposal of these products in landfills by an uninformed population represents an important potential environmental Hg contamination route (D'Itri, 1972b).

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[1] Authors: R. A. Griffin and G. D. Robinson

There has been very little research done on the chemical behavior of Hg in municipal leachates. The information that is available to date on Hg in municipal leachates is insufficient to evaluate the migration of Hg in landfills. It is therefore our purpose here to report the results of studies on the adsorption of Hg from leachate by clay minerals. These studies were initiated to determine whether or not clay minerals have potential for use as landfill liners for attenuation of Hg which may be present in leachates.

EXPERIMENTAL

In order to determine the amount of Hg removed from solution, a series of samples were prepared using $HgCl_2$ in DuPage landfill-leachate, and $HgCl_2$ in DuPage landfill-leachate with clay (kaolinite or montmorillonite) added. The latter two treatments were also used to determine the amounts of organic and inorganic Hg removed from solution.

The amounts of organically-bound Hg and inorganic Hg in solution were determined by the flameless Atomic Absorption Spectroscopy (AA) technique described in the appendix.

Eight samples were prepared for each solution in each experiment. Before addition of Hg, 50 ml aliquots of either deionized-H_2O, DuPage leachate, or DuPage leachate and 1.000 g kaolinite were added to 125 ml Erlenmeyer flasks. The pHs of the solutions were then adjusted using 0.1N, 1N, 3N, and/or conc. HNO_3 to obtain pH values between 1 and 9 (each set of samples spanned this range). The samples were placed in a shaking waterbath at 25 ± 0.5° C, and allowed to equilibrate overnight. The pH values were checked after 20-24 hours and 2 ml aliquots of 25 ppm Hg stock solution were added to each flask giving a total volume of 52 ml and a Hg concentration of approximately 0.962 ppm. The samples were again placed in the shaking waterbaths and allowed to equilibrate overnight. After 20 to 24 hours the final pH values of the samples were recorded, and each sample was transferred to a 50 ml centrifuge tube and centrifuged at 20,000 rpm for 5 minutes. The supernatant solutions were decanted, acidified, and analyzed for their Hg content using flameless AA.

The amount of Hg removed from solution by a given clay at a particular pH was determined as follows:

$$C_R = \frac{(C_I - C_{Eq}) \times V_F}{W} \qquad \{19\}$$

where C_R = amount of Hg removed in μg/g clay.
C_I = initial Hg concentration in ppm,
C_{Eq} = equilibrium Hg concentration in ppm,
V_F = total solution volume after pH adjustments in ml, and
W = weight of clay in grams.

The amount of Hg removed from solution was then plotted as a function of pH.

RESULTS AND DISCUSSION

Some examples of results obtained for Hg removal from various solutions plotted as a function of pH are presented in Figure 41. It can be seen from this figure that Hg is removed from solution, even from a presumably sterile and pure $HgCl_2$ solution (curve A). In the short time available for this study we were not able to satisfactorily isolate all the reasons for this removal of Hg. Three possible removal mechanisms are adsorption onto the walls of the glassware and plastic bottles, precipitation, or volatilization. At the lower pH values the Hg removal is thought to have been by adsorption onto the glassware, although standard solutions may be satisfactorily stored at pH 2. It is presumed that the adsorption in the sample solutions occurred at the higher initial pH values and that the Hg did not have sufficient time to totally desorb after the pH was adjusted to lower values. The increase in removal in the higher pH range (5-8) is apparently the result of both precipitation and adsorption. Volatilization was not considered as an important mechanism for the Hg losses observed from the $HgCl_2$ solutions since they were presumably sterile and stoppered.

An increasing amount of Hg removal is displayed in curve B (leachate blank) which illustrates the loss of Hg from a leachate solution. The removal of Hg from solution here is again probably due to the same mechanisms; that is, the increase in Hg removal (greater amount of Hg removed by leachate than by deionized-H_2O) is probably the result of either increased adsorption or increased precipitation. However, volatilization losses of organic Hg compounds due to microbial transformations in the leachate are also possible.

Curve C in Figure 41 shows the total amount of Hg removed from leachate with 1 g of kaolinite present. The amount of Hg removed by 1 g of kaolinite is taken as the difference between curve C and curve B in Figure 41. This is plotted as curve B in Figure 42.

Figure 42 shows a breakdown of various forms of Hg removal from leachate solutions. The amount of organic- and inorganic-Hg removed by clay was determined by placing an aliquot from each sample into each of two BOD bottles. One set was digested following the general procedure while the second set was analyzed undigested. A set of leachate blanks was treated in the same manner. There were then four separate sets in all, which included a digested blank ($HgCl_2$ in leachate), an undigested blank, a digested sample ($HgCl_2$ in leachate with 1 g kaolinite), and an undigested sample.

The total organic-Hg in solution was determined by taking the difference

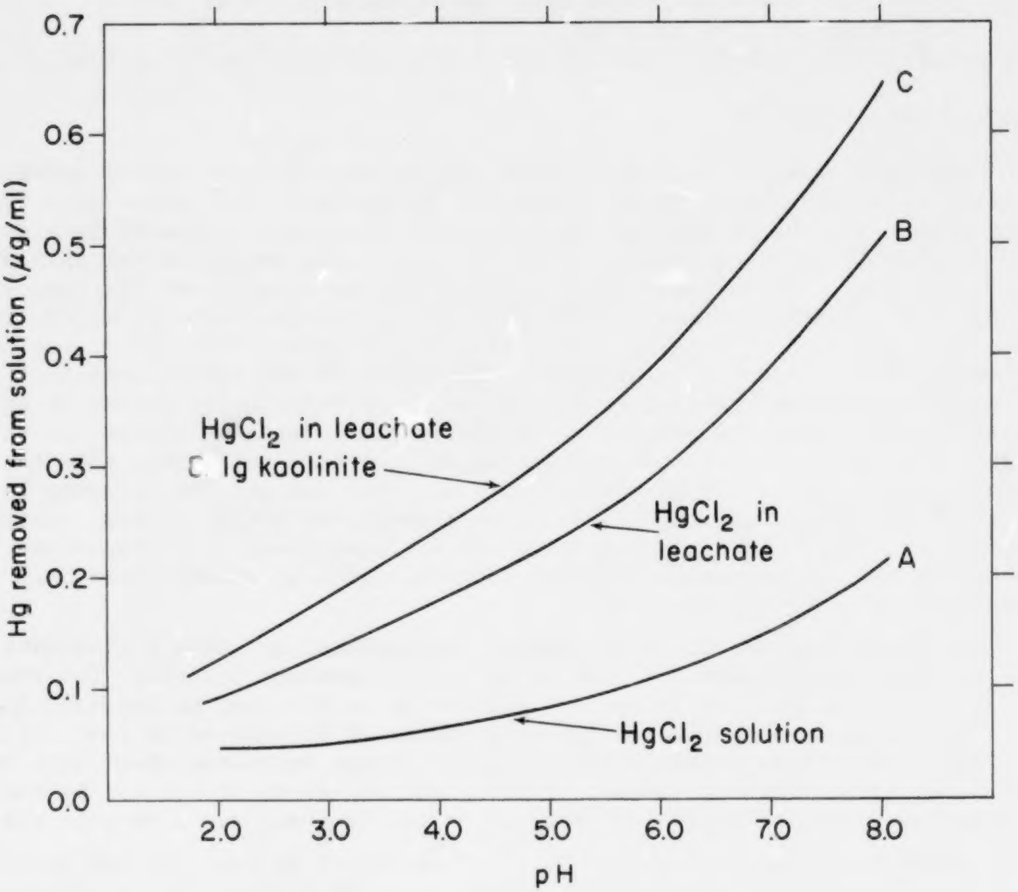

Figure 41. Removal of Hg from DuPage landfill-leachate and pure $HgCl_2$ solutions plotted as a function of pH at 25° C. The initial Hg concentration is 0.96 ppm and the final volume is 52 ml.

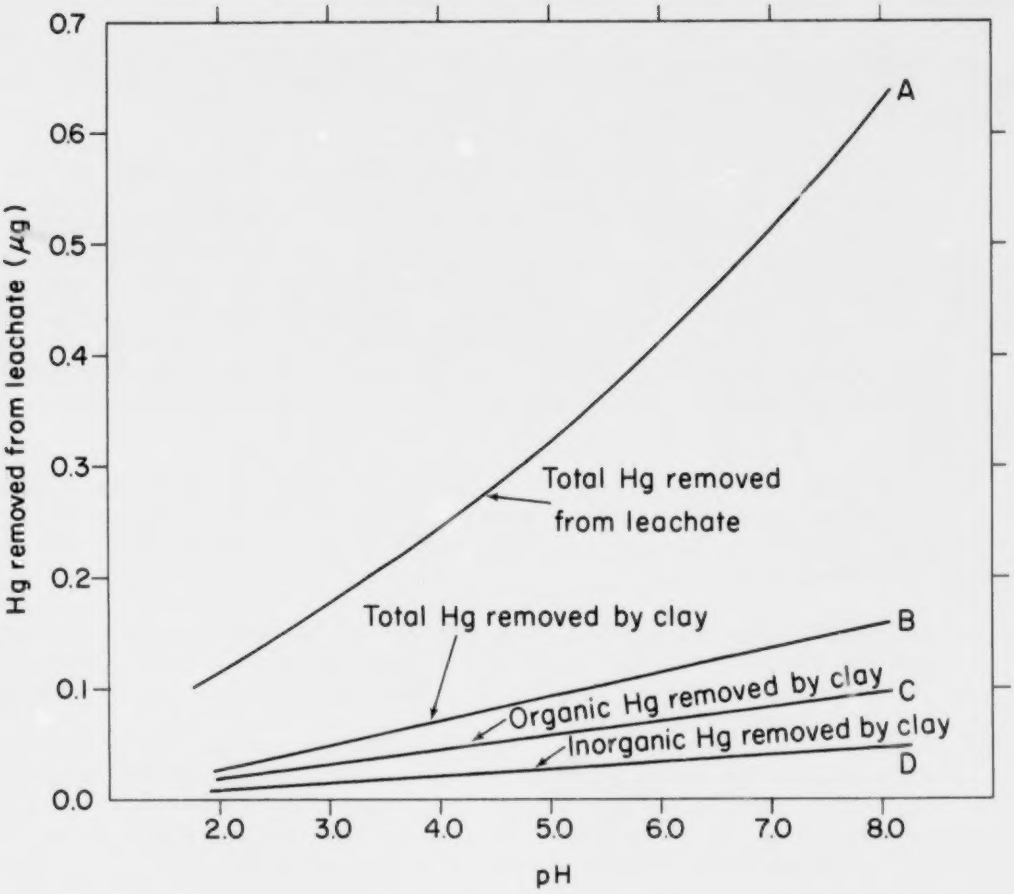

Figure 42. Removal of various forms of Hg from DuPage landfill-leachate solutions by kaolinite plotted as a function of pH at 25° C.

between the digested and undigested blanks. The amount of organic-Hg in solution with 1 g kaolinite present was always less than the organic-Hg determined from the blanks. This difference was then taken as the amount of organic-Hg removed due to the presence of the clay. Figure 42 illustrates the relative amounts of organic-Hg (curve C) and inorganic-Hg (curve D) removed by 1 g kaolinite plotted as a function of pH. These results can be compared to the total Hg removed by 1 g kaolinite in curve B and with the total Hg removed from solution by all mechanisms in curve A.

The results given in Figure 42 illustrate that the Hg removal is pH dependent, with increasing amounts of removal as the pH is raised within the range 2 to 8.

From the data, it can be stated that approximately two thirds of the total Hg removed by 1 g kaolinite was organic Hg (curve C), while about one third of the Hg removed by the clay was inorganic Hg (curve D). The total Hg removed from solution (curve A) is apparently the result of several mechanisms operating simultaneously, i.e. adsorption by clay, volatilization, and precipitation. The amount of Hg removed as a result of the presence of clay was evaluated, as previously described, and accounted for approximately 20 to 30% of the total Hg removed from solution. It therefore appears that precipitation and volatilization account for the largest amounts of Hg removed in this study.

At this time, no data is available as to the relative amounts of Hg lost by volatilization from the leachate as opposed to precipitation. In any event, large amounts of Hg are lost from leachate solutions both in the presence and absence of clay.

In an unreplicated experiment, the removal of Hg from solution by montmorillonite was found to be approximately 5 times greater than the removal of Hg from solution by kaolinite. Since this experiment has not been repeated, the results are tentative. However, this ratio is similar to the ratio of the Cation Exchange Capacities (CEC) of these two clay minerals. Since this result is consistent with those for the previous heavy metal cations studied, it was concluded that the difference in adsorption between montmorillonite and kaolinite was due to the cation exchange of the various ionic forms of Hg which may be present in leachate solutions of variable pH.

CONCLUSIONS

The results of this study indicate that removal of Hg from leachate solutions is enhanced by clay minerals and is pH dependent. Substantial amounts of Hg were removed from leachate by the clays, and these amounts were concluded to be in proportion to the respective CEC values of the clays. Of the amount of Hg removed by the clays, it was concluded that about two thirds was organic Hg and one third inorganic Hg.

Large amounts of Hg were removed from solution, both in the presence and absence of clay. These results lead to the conclusion that adsorption by clays was not the major mechanism responsible for removal of Hg. Rather, precipitation and/or volatilization accounted for between 70 and 80% of the Hg removed from the leachate solutions and were concluded to be the predominant attenuation mechanisms in these experiments.

The results of this study suggest that maximum removal of Hg from leachate would be achieved by disposal under alkaline conditions. It is also suggested that montmorillonitic clays or soils will remove substantially more Hg than kaolinitic clays or soils.

SECTION 12

SUMMARY OF ADSORPTION STUDIES

The results of these studies with heavy metals indicate that pH has a pronounced effect on the amounts adsorbed from landfill leachates by clay minerals. It was concluded that the principal adsorption mechanism is cation and anion exchange, a mechanism that led to the strong pH dependency of the adsorption process. In addition, species distribution diagrams led to the conclusion that it is the monovalent species of each element that is principally adsorbed by anion exchange.

A comparison of the relative amounts of heavy metals removed at pH 5.0 from 100 ppm equilibrium concentration solutions of the metals studied, both cationic and anionic, is presented in Table 14. The table indicates that the cationic heavy metals are generally adsorbed to a greater degree than the anionic forms. However, this ranking is somewhat pH-dependent, because the greatest anion adsorption occurs in acid solutions and the greatest cation adsorption in alkaline solutions. The ranking therefore changes somewhat at different pH values.

A significant point shown in Table 14 is the importance of the valence state of an element to the amount of that element removed from solution by clay minerals. Cr(III) species are removed to a much greater extent than Cr(VI) species. The clay minerals removed 30 to 300 times more Cr(III) from solution than Cr(VI). The table also shows more extensive removal of As(V) than of As(III). These results indicate that safer disposal of certain elements may be achieved if, prior to deposition at the landfill or disposal site, the element is converted to the form that would be most strongly attenuated.

The information derived from the studies of the various elements indicatesthat the amounts of heavy metals removed from leachate by clay minerals depends to a large degree on the element and the form of the element involved, the pH of the leachate, the adsorption capacity of the particular clay mineral in the liner, and the ionic strength of the leachate.

The adsorption capacity of the clay minerals and the reversible nature of exchange-adsorption reactions have important environmental consequences. For example, if industrial wastes containing heavy metals are placed in a landfill, changes in the ionic composition or pH of the leachate can occur. A change in pH may release large amounts of potentially toxic heavy metals into the aqueous phase, especially in places where precipitates may have accumulated. Other ions in the waste compete with the heavy metals and may

TABLE 14. REMOVAL OF HEAVY METALS FROM SOLUTIONS BY KAOLINITE AT pH 5.0

Element	Amount removed at equilibrium concentration of 100 ppm (μmoles/g)	
	Pure solutions	Du Page leachate
Cr(III)	769*	576*
Cu	55.1	15.7
Pb	42.3	12.1
As(V)	†	5.3
Zn	33.6	3.8
As(III)	‡	2.0
Cd	26.7	1.9
Se	†	1.9
Cr(VI)	0.62	1.9

*Precipitation contributes to removal at pH 5.0.

†Removals from 40 ppm solutions were approximately the same as removals from leachate.

‡Removals from 40 ppm solutions were 30 percent greater than removals from leachate.

exchange with them, thus allowing metal ions to come into solution. These multiple interactions must be considered when a disposal site is designed and when the environmental impact of adding heavy-metal wastes to municipal landfills is assessed.

SECTION 13

APPLICATION OF THE RESULTS TO THE PROBLEM OF LANDFILL DESIGN

LANDFILL DESIGN

Regarding pollutant control, the design of a landfill should take into account three factors: the hydrologic system governing direction of pollutant travel, the geochemistry of the water-sediment system, and the release rate of unattenuated pollutants to surface or ground waters. The first item has been the subject of a number of papers and will not be addressed here.

Current landfill design and engineering practice are to construct clay liners, either natural or artificial, very thick and containing high clay percentages. The motive is to create relatively impermeable liners that will contain the leachate and therefore protect the groundwater resources. This approach can create difficulties in humid climates where infiltration exceeds the capacity of the liner to dissipate the leachate. This causes what is referred to as the "bathtub" effect wherein the relatively impermeable clay liner acts as a bathtub which fills up with leachate and then overflows. If the leachate is not collected and treated, the overflow manifests itself in the form of leachate springs on the surface and results in surface water pollution and surface environmental degradation instead of ground water pollution. Neither form of pollution is desirable; both might be prevented by using proper design features in the construction of the sanitary landfill. If one does not choose to collect and treat the leachate and wishes to avoid the "bathtub," the results of this research suggest an alternative landfill design.

The chemical attenuation study reported in Section 5 has indicated that most of the toxic constituents found in municipal leachates are moderately-to-highly attenuated by passage through laboratory columns containing relatively low percentages of clay minerals. If the assumption is granted that the "bathtub" effect is an undesirable feature of clay liners, then it follows that it is desirable to determine the point of "optimal" attenuation, i.e., the percentage of clay in a liner material which gives the maximum attenuation balanced with a maximized hydraulic conductivity. Figure 43 represents a dual scaled graph with the initial hydraulic conductivity of the montmorillonite columns as given in Table 3 plotted as a function of percentage of montmorillonite. The opposite scale is the attenuation number for the chemical constituent of interest also plotted as a function of the percentage of montmorillonite. The attenuation numbers (Table 5), as reported in Section 5, are the percentage of removal of the element from the leachate upon passage through 10 pore volumes of the clay-sand mixture. The attenuation

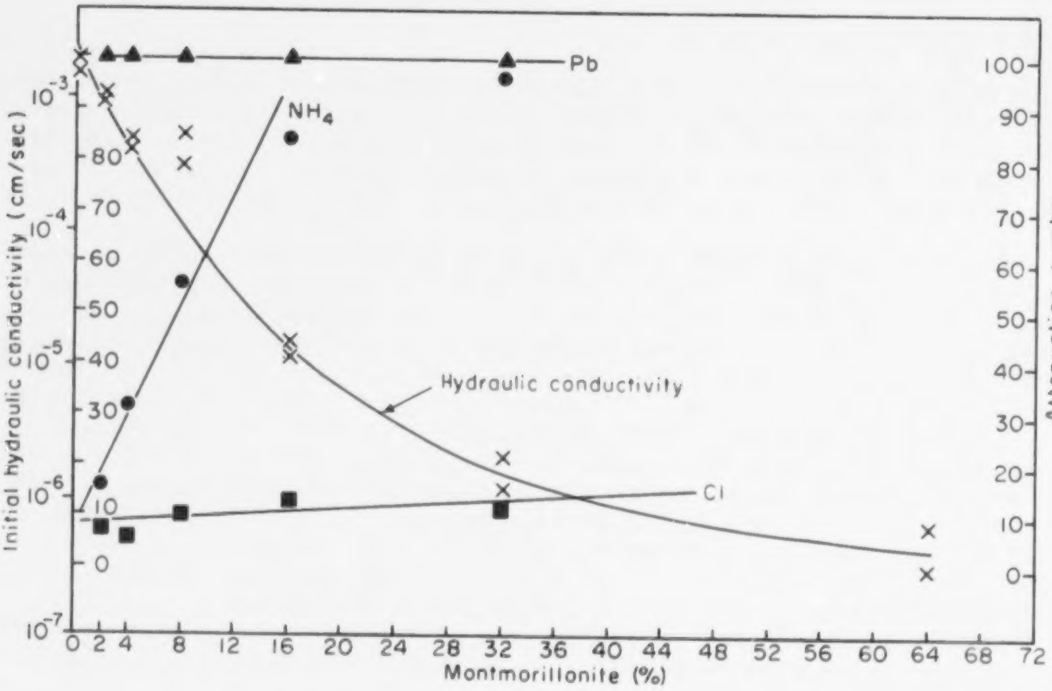

Figure 43. Effect of clay content on hydraulic conductivity and attenuation of Pb, NH$_4$, and Cl for a 40-cm thick liner. The bulk densities vary; densities for each clay content are shown in Table 3.

number scale is given as 0 at the point of minimum hydraulic conductivity and 100 at the point of maximum hydraulic conductivity.

For the heavy metals (Pb is used here as an example), even small amounts of clay gave almost total removal. The heavy metals, even though toxic, represent a minimal pollution hazard in municipal leachates because they are attenuated very strongly and are usually present at low levels in leachates. Therefore they can usually be ignored as far as determining the optimal clay liner for a given leachate. At the other extreme are the relatively non-interacting constituents represented by Cl. Chloride as shown here is relatively unattenuated by even large amounts of clay. Figure 43 suggests that in order to prevent chloride migration, relatively impermeable clay liners would be necessary. Due to the non-toxic nature of the chloride ion, it also ranks low along with the heavy metals in the pollution hazard index (Table 6). In view of the problems associated with the "bathtub" effect, it seems unwise to design clay liners to optimize chloride attenuation. Rather, it seems prudent to design clay liners for optimum attenuation of the most hazardous constituents found in a particular leachate. In the case of the DuPage leachate used in this study, the pollution hazard index ranks NH_4^+ as 30 times more of a pollution hazard than any other constituent found in this leachate. It therefore seems reasonable to design a clay liner for DuPage leachate that gives optimal attenuation of NH_4^+ and all the other constituents should also be attenuated to relatively safe levels for minimal pollution of the groundwaters adjacent to the landfill site.

For the case of NH_4^+ (shown in Figure 43) if one extrapolates the curve, it is apparent that 18-20% montmorillonite would give nearly total removal from the leachate. If the 10% liner is doubled in thickness from the 40 cm used in this study to 80 cm, it will contain enough montmorillonite to give nearly total removal of the NH_4^+ in 10 pore volumes of leachate and still retain the relatively high hydraulic conductivity of 6×10^{-5} cm/sec. This illustrates that, for a given desired hydraulic conductivity, the removal capacity of the liner may be adjusted by changing its thickness (at the same clay content) without greatly affecting transmission of water through it.

LINER THICKNESS

The thickness of various mixtures of sand and clay, as represented by the total cation exchange capacity (CEC), to achieve total attenuation of selected relatively mobile ions was calculated (Table 15). The removal efficiency will differ in leachates, depending upon relative ion strength. The efficiencies used in Table 15 are based on the DuPage leachate used in this study. The concentrations are given in parentheses under the average concentration value. Increasing cation exchange capacity generally reflects increasing clay contents. Thus a thicker liner with greater hydraulic conductivity and lower CEC may be the optimal liner for attenuation.

Determining the release rate of nonattenuated or poorly attenuated contaminants from the clay liner (natural or man-made) to surface waters or ground-water aquifers is necessary for good landfill design. In designing a landfill, a decision must be made as to which ions should be totally attenuated

TABLE 15. ESTIMATED LANDFILL LINER THICKNESS NECESSARY FOR ATTENUATION OF SOME LEACHATE CONSTITUENTS PER CUBIC METER OF REFUSE DURING A 20 YEAR FILL LIFE*

Constituent	Initial** Concentration		CEC					
			10		20		30	
	Ave. (ppm)	Max. (ppm)	Ave. (cm)	Max. (cm)	Ave. (cm)	Max. (cm)	Ave. (cm)	Max. (cm)
NH_4	379 (830)	1,106	32	92	16	46	11	31
Na	755 (740)	7,700	118	1,208	59	604	39	403
K	763 (530)	3,770	51	252	26	126	17	84
Mg	1,609 (240)	15,600	226	2,191	113	1,096	75	730

*Assumption: Bulk density = 1.8 g/cc; 100 liters of leachate generated per m^3 of refuse/yr.; initial concentration decreases linearly to zero at 20 yr.; removal efficiencies for each constituent were estimated using the average values given by Griffin, et al. (1975), NH_4 = 37.1%, Na = 15.4%, K = 38.2%, Mg = 29.3%.

**Concentrations taken from the twenty leachate analyses reported by EPA (1974); those in parenthesis, (830), are the values of Old DuPage landfill leachate used in this study.

and which should be eventually released to the environment. The chloride ion, which moves essentially unattenuated, is the most obvious example of the latter type.

CONCLUSIONS

The results of this study suggest an alternative to landfill design. The use of hydraulic conductivity information and the pollution hazard rating for a given leachate or waste stream can allow a different approach than the prevalent "containment" type liner systems. These data suggest that overall pollution would be lessened by designing landfill liners for higher permeability and by selectively attenuating the most toxic pollutants from leachate and allowing the groundwaters to dilute the nontoxic components which can be tolerated at much higher concentrations than the toxic without deleterious effects. Thus landfill stabilization and use for other productive purposes could be achieved at much faster rates than can presently be achieved by containment type liners.

SECTION 14

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APPENDIX A

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APPENDIX B

PROCEDURES USED IN CHEMICAL AND PHYSICAL CHARACTERIZATION OF CLAY MINERALS AND LIQUID SAMPLES

Clay Mineral Characterization

(W. A. White)

The kaolinite used in this study was collected from materials of Pennsylvanian age in Pike County, Illinois. The site description and location are given by White (1959), sample 996N. The montmorillonite used in the study was southern bentonite from the American Colloid Company. The illite was from the Minerva Company Mine of the Allied Chemical Company.

The clays were brought to the laboratory, where they were crushed, ground, and purified by sedimentation techniques to obtain the <2 µm particle fraction that contained essentially pure clay minerals. The purified clay was then floculated with 1 M $CaCl_2$, centrifuged, and spray dried. The clay minerals present in the <2 µm fraction were identified by X-ray diffraction techniques (Parham, 1962), and the results are given in Figure 44. The positions of the diffraction peaks identify which clay minerals are present in the sample. In addition, the areas under the peaks of the diffraction patterns give a crude estimate of the relative amounts of each clay mineral in the sample and were used to prepare the following summary:

(a) The montmorillonite sample was found to be almost completely monomineralic, containing approximately 95% montmorillonite and 5% mixed-layer materials close to montmorillonite in composition.

(b) The illite sample was found to be monomineralic, with mica minerals predominant. The sample contained approximately 70% illite and 30% mixed-layer materials close to illite composition.

(c) The kaolinite sample could be characterized as a moderately pure kaolinite, comparable to the Georgia hard kaolins. The sample contained approximately 87% kaolinite, 8% illite, 5% mixed-structure material, and a trace of quartz.

Atomic Absorption Methods for Cd, Fe, Mn, Pb, Si, Zn, Na, K, Ca, and Mg

(John Steele and David Heck)

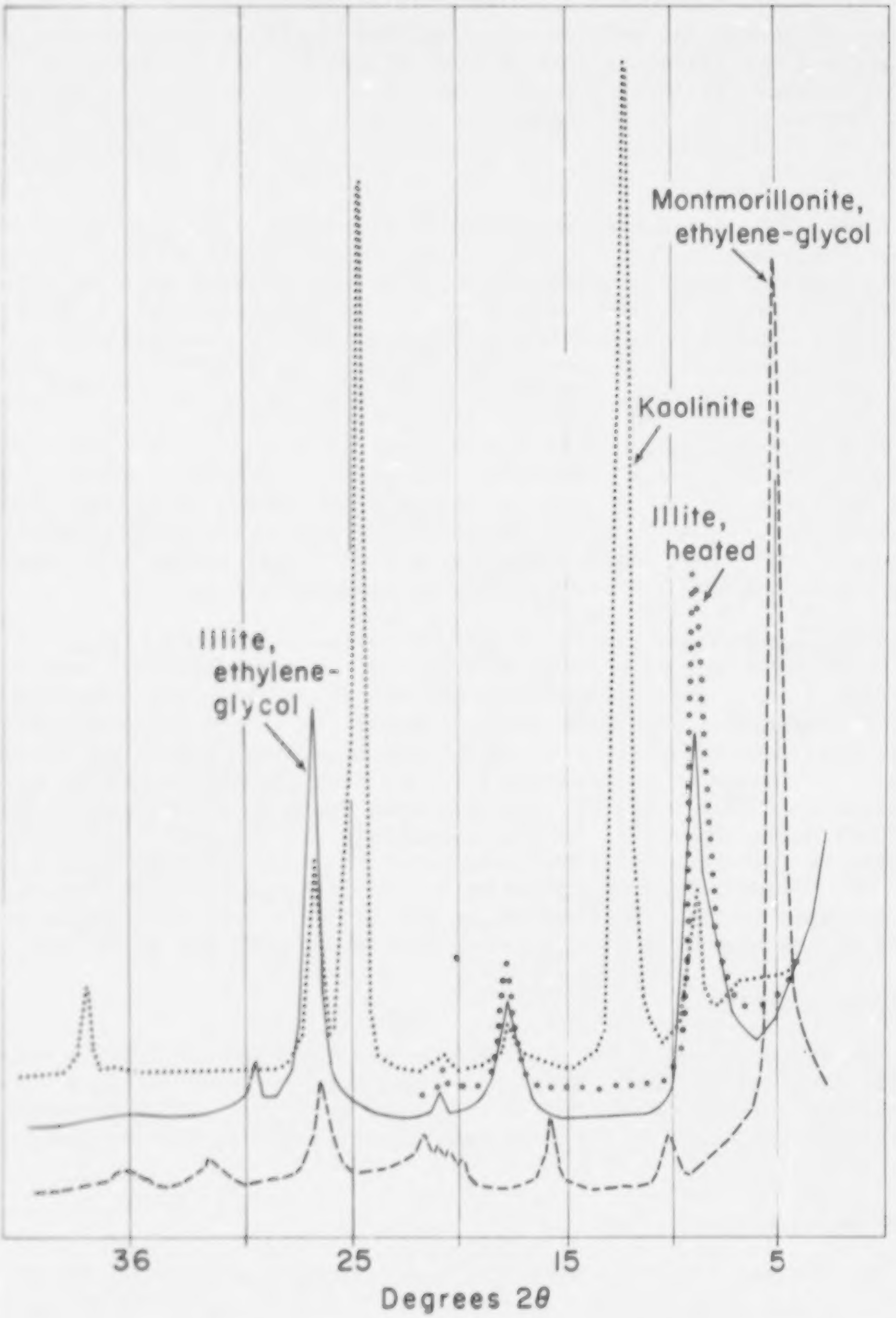

Figure 44. X-ray diffraction patterns of the clay minerals used in leachate pollutant attenuation studies.

Atomic absorption methods were used for the following determinations: filtered and acidified leachate (dissolved metals) -- Cd, Fe, Mn, Pb, Si, and Zn; membrane filters (suspended metals) -- Cd, Fe, Mn, Pb, and Zn; ammonium acetate extracts (exchangeable cations) -- Cd, Fe, Mn, Pb, Zn, Na, K, Ca, and Mg; and column sections and original clays (total cations) -- Cd, Mn, Na, Pb, and Zn.

Atomic absorption measurements were made using a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer. In the case of the dissolved, suspended, and exchangeable metal determinations, measurements were recorded directly from the electronic digital readout in the auto-concentration mode. For the total cation determinations, absorbance measurements were recorded on a Perkin-Elmer Model 056 Recorder. The following Perkin-Elmer burner heads were used: a 4-inch-long slot, flat-head burner using an air-acetylene flame for all of the dissolved and suspended cation determinations except Si; a 2-inch-long slot nitrous oxide burner head using a nitrous oxide-acetylene flame for Si determinations; and a three slot high solids burner head with an air-acetylene flame for all of the exchangeable and total cation determinations. Standard single element hollow cathode lamps were used. Corrections for background absorption were made simultaneously for total cation determinations using a Perkin-Elmer Deuterium Arc Background Corrector.

All reagents used are ACS certified reagent grade chemicals, and standard stock solutions were prepared from high purity metals or compounds. Calibration standards prepared from diluted stock solutions contained the following matrices: dissolved metal standards -- 1% v/v distilled HNO_3; suspended metal standards -- 4% v/v distilled HCl; exchangeable cation standards -- 1 N ammonium acetate and 7.5% v/v distilled HNO_3; and total cation standards -- 1.2% v/v 48% HF, 1.5% v/v aqua regia (1:3:1 HNO_3-HCl-H_2O), and 0.54% w/v H_3BO_3. For total Na determinations, the standards contained, in addition to the above mentioned matrix for total cations, 1000 ppm Cs as CsCl. For determination of Ca and Mg in the leachate fraction, the standards were prepared to contain 1% w/v La_2O_3 and 2.5% v/v HCl. For determination of Na and K, the standards were prepared to contain 1000 ppm Cs as CsCl.

Sample preparation

The filtered-and-acidified leachate and the ammonium acetate extract samples required no sample preparation and were analyzed directly except that for the analysis of Ca and Mg, 1% La_2O_3 w/v and 1% v/v HCl were added. Also for the determination of K and Na, the final sample contained 1000 ppm Cs as CsCl.

Column section dissolution

The methods described below are modifications of those of Bernas (1968) and French and Adams (1973). Approximately 0.5 g of the clay-sand mixture, previously dried at 110° C for several hours, is transferred to a 125 ml linear polyethylene screw cap bottle. The sample is wetted with 1.5 ml aqua regia, and 1.2 ml of 48% HF is added. The cap is screwed tight, and the bottle is placed in a steam bath for 2 hours. The sample and acids are mixed by an occasional swirling of the bottle during this period. The bottle is removed from the steam bath, and 9 ml of a H_3BO_3 solution (0.06 g/ml) is added to the sample to complex the fluoride. The bottle is again sealed and placed on the steam bath for 0.5 hours, removed, and allowed to cool. The dissolved sample is transferred to a 100 ml polyethylene volumetric flask, the bottle is washed repeatedly with deionized H_2O, and the washings are added to the flask. The sample is diluted to volume with deionized H_2O and returned to the polyethylene bottle for storage.

Membrane filter dissolution

The membrane filters were treated according to methods modified from Parker (1972). The membrane is placed in a 250 ml Pyrex beaker, and 3 ml of distilled HNO_3 is added. The beaker is covered with a watch glass and heated on a hot plate where the acid is evaporated to dryness. The additions of acid and the heating steps are continued until a light residue is left. The residue is taken up with 2 ml of distilled 1:1 HCl and warmed gently. The sample is then transferred to a 50 ml Pyrex volumetric flask, and the beaker is washed repeatedly with small portions of deionized H_2O and the washings added to the flask. The sample is diluted to volume and transferred to a polyethylene bottle for storage.

Atomic Absorption Spectrophotometric Procedures

The following analytical wavelengths were used: 228.8 nm (Cd), 248.3 nm (Fe), 279.5 nm (Mn), 589.0 nm (Na), 283.3 nm (Pb), 251.6 nm (Si), 213.9 nm (Zn), 422 nm (Ca), 285 nm (Mg), and 766.5 nm (K). Where necessary, samples are diluted to bring the metal concentration within the linear portion of the calibration curve. For total Na determinations, samples are diluted 1 to 2 with the addition of 1000 ppm Cs as CsCl. In the case of the suspended, dissolved, and exchangeable metal determinations, the metal ion concentrations are determined directly from the electronic digital readout in the auto-concentration mode, after appropriate calibration. For the total cation determinations, the metal ion concentrations are calculated by solving for concentration in a least squares constructed calibration equation of absorbance vs. concentration. A new calibration curve equation is calculated for each set of analyses.

An estimate of the average relative standard deviation for the elements determined by atomic absorption spectrophotometry is 10 percent or better.

Determination of Hg by Flameless Atomic Absorption

(R. A. Griffin and G. D. Robinson)

The Hg samples obtained in the investigation of the removal characteristics of Hg from leachate solutions by clay minerals as a function of pH were analyzed by flameless Atomic Absorption Spectroscopy (A.A.) using a slight modification of the procedure described by the U. S. Environmental Protection Agency (EPA) (U.S.-EPA, 1971).

Variations of the standard procedure described by U.S.-EPA (1971) were implemented in order to gain maximum sensitivity from the procedure and the available instrumentation. The apparatus used was a Perkin-Elmer Model 360

A. A. equipped with a Perkin-Elmer Flameless Mercury Analysis System. The absorption cell supplied by Perkin-Elmer was modified by replacing the plastic end windows with quartz windows which were glued in place with epoxy cement. This allowed greater light transmission and higher sensitivity and stability to be achieved for the Hg analyses.

Reagents used:

Sulfuric Acid reagent grade conc.
Nitric Acid reagent grade conc.
Potassium Permanganate 5% w/v 5g $KMnO_4$ in 100 ml DI H_2O
Potassium Persulfate 5% w/v 5g $K_2S_2O_8$ in 100 ml DI H_2O
Hydroxylanine Hydrochloride 5% w/v 5g $NH_2OH \cdot HCl$ in 100 ml DI H_2O
Stannous Chloride - Dissolve 50g $SnCl_2$ in 100 ml conc. HCl and 400 ml DI H_2O
Stock Mercury Solution 1000 ppm - Dissolve 1.080g HgO in min. vol. 1:1 HCl - dilute to 1 liter with DI H_2O
Working Mercury Solutions - Make successive dilutions of the stock Hg solution to obtain a standard containing 0.1 ppm. This should be made fresh daily and acidified to .15% HNO_3. Note: It was found that 10 and 25 ppm working Hg standards could be stored in plastic bottles several weeks if acidified to .15% HNO_3 with no apparent loss or adsorption of Hg. This greatly reduced the steps involved in making fresh working standards of .1 ppm.
Waste Hg Absorbing Media - .1 M $KMnO_4$ and 10% H_2SO_4.

A calibration curve was obtained following the procedure outlined in U. S.-EPA (1971) substituting a hydroxylamine-HCl solution for the hydroxylamine sulfate solution, and a stannous chloride solution for the stannous sulfate solution. It was found that this calibration curve had to be repeated with each set of samples.

The samples for Hg analysis were placed in 60 ml plastic bottles and acidified with conc. HNO_3 to pH ~2. A 1 ml aliquot was then taken from each sample and placed in a 300 ml BOD bottle (these were run in triplicates); the volume in the bottle was then brought up to 100 ml with DI H_2O. The samples were then digested to oxidize the organo-mercury compounds which would not otherwise respond to the flameless A. A. technique (U. S.-EPA, 1971).

The samples were digested by addition of conc. H_2SO_4 and 2.5 ml of conc. HNO_3 to each bottle with mixing after each addition. One ml of 5% w/v $KMnO_4$ solution was then added to each bottle, swirled, and allowed to stand for at least 15 minutes. Two ml of $K_2S_2O_8$ were then added and allowed to stand for at least 30 minutes. Two ml of $NH_2OH \cdot HCl$ were then added to each bottle to reduce the excess permanganate. Immediately prior to aerating through the absorption cell, 2 to 3 ml of $SnCl_2$ solution were added to each bottle. The samples were read on the absorbance mode and then converted to concentration mathematically using linear regression analysis (calibration standards were prepared fresh daily). The final Hg concentrations were then subtracted from the initial concentration (0.962 ppm) to obtain the amount of Hg removed from solution.

Neutron Activation Analysis Methods for Hg and As

(Joyce Frost and Larry Camp)

Irradiations are carried out in the University of Illinois' Advanced TRIGA reactor, with a thermal neutron flux of 1.4 x 10^{12} neutrons cm^{-2} sec^{-1} (500 KW). The samples are contained in a rotary specimen assembly. Rotation at 1 rpm during irradiation ensures an equivalent integrated flux for each sample.

Samples and standards are irradiated in heat-sealed polyethylene snap-cap vials which were previously cleaned with deionized water and acetone.

The gamma-ray spectrometer system consists of a 3" x 3" NaI(Tl) crystal connected to a 400-channel analyzer. The analyses are comparative -- e.g. the activity of an element in the sample is compared to that of the element in a known standard to determine concentration of the element in the sample.

Determination of Hg by Instrumental Neutron Activation Analysis in "Spiked" Liquid Samples

This procedure was used for the column effluent samples (filtered and acidified leachate samples), solubilized membrane filter samples, and ammonium extract solutions of the clay column samples that originated after the original sterile leachate was spiked with mercury to a resulting concentration of 4.0 ppm.

A two-hour irradiation was carried out on 5 ml portions of the samples and two acidified mercuric nitrate standards, one containing 5.02μgHg/ml and the other 0.502μgHg/ml. The samples were left to decay one week to decrease interference from short-lived radioisotopes, especially 15 hour ^{24}Na and 36 hour ^{82}Br which gives a high background in the low energy region of the gamma ray spectrum. The activity in the samples and standards due to the 0.077 MeV gamma ray of 65 hours ^{197}Hg was then counted. At the same time uranium was determined in those column effluent samples that unexpectedly had a high concentration of uranium, up to 0.20 ppm; these were the first several sets of effluents collected from the columns that contained montmorillonite. The uranium activity counted was the 106.1 keV gamma ray of 56.4 hour ^{239}Np; the standard was 5 ml of a solution of $UO_2(NO_3)_2$ containing 1.02 μg U/ml.

Determination of Hg in Liquid Samples by Neutron Activation Analysis with Radiochemical Separation

This procedure was used for the original leachate and for the precise determination of mercury in some of the samples having a low mercury content.

The method follows closely that of Weiss, Koide and Goldberg (1971). The samples (1 to 3 irradiation vials, each containing 10 ml per sample) and standard (10 ml of 5.02μgHg/ml) were irradiated for 2 hours. After a day's decay, each sample was transferred to a beaker, and 10 mg of Hg^{++} carrier was added. The pH of the solution was adjusted to 1 and elemental mercury precipitated by the addition of stannous chloride solution. The mercury was separated on a Millipore filter and dissolved in aqua regia. This solution was neutralized with ammonium hydroxide, and thioacetamide solution was added. The precipitate of mercuric sulphide was separated on a Millipore filter; dissolved in aqua regia; transferred to a tared, glass, stoppered vial; and made up with deionized water to 25 ml. The activity of the solution due to the 0.077 MeV gamma ray of ^{197}Hg was counted. The radiochemical separation for the standard (250 µl) plus carrier was begun with the mercuric sulphide precipitation step. Radiochemical yields (85-98%) were determined by re-irradiation of a 1 ml aliquot of each sample and the standard.

Determination of Hg in Column Sections and Clay

One gram of sample was accurately weighed and irradiated for two hours as previously described. The irradiated sample was then mixed with ~1 gram of Alundum and transferred to a combustion boat which has had Hg carrier added as $Hg(NO_3)_2$. The boat was then placed in a Vicor tube which in turn is placed in a Lindberg "Heavy Duty" furnace, such that O_2 can flow through and the combustion gasses trapped in a dry ice cold trap. The furnace is operated for 15 minutes at 1000° C and allowed to cool.

The boat was removed from the cooled tube (at most, 400° C) and the cold trap section (dry ice removed) placed end down into a polyethene 100 ml centrifuge tube.

The foresection of the tube was washed with 10 ml of HNO_3, and this solution via transfer pipplets was used to wash down the cold trap section of the tube. This was repeated twice more, but H_2O substituted for the HNO_3, giving 30 ml of total solution. The centrifuge tube was placed in H_2O bath and heated. When hot (90° C or +), the solution was stirred and solid NH_4Br (AR) added, red Br_2 was evolved, and the solution was stirred. Solid $Ag(NO_3)_2$ was added to remove the excess Br (much of the radioactive Br had isotopically exchanged) and the solution was centrifuged. The liquid was transferred to a 4 oz. wide mouth jar and labeled.

Ten ml of warm (90+° C) HNO_3-H_2O (1-3) was added to the ppt in tube and again centrifuged. This solution was added to the original 30 ml, and the solution counted for 77.6 KEV γ ray of Hg^{197} (65.5 hour $t_{\frac{1}{2}}$) on a NaI detector. One ml of this solution was removed and put in 1 dram vial, sealed, and labeled and irradiated at 15 minutes at 500 KW. This was compared with a "carrier vial" and a "yield" factor found for correction.

Determination of Arsenic in Liquid Samples by Neutron Activation Analysis with Radiochemical Separation

Ten ml of sample and 10 ml of an arsenic trioxide standard were irradiated for 1 hour, then left to decay for a day. The sample with 30 mg of As^{+++} carrier added, in a distillation flask, was oxidized by boiling it for 5 min. with 3 ml of 30% H_2O_2, to decompose organic arsenic compounds present (EPA, 1971). Then, after the addition of hydrochloric and hydrobromic acids, arsenic was distilled from the solution (NAS-NS #3002, 1965). Elemental arsenic was precipitated from the distillate by the addition of sodium hypophosphite. The precipitate was separated on a weighed filter paper, reweighed, and the activity due to the 0.56 MeV gamma ray of 26.5 hour ^{76}As was counted. The standard was carried through the same radiochemical separation.

Determination of Arsenic in Clay Samples by Neutron Activation Analysis with a Radiochemical Separation

The procedure followed was that used by Ruch, Kennedy and Shimp (1970) for the determination of arsenic in sediments. The irradiated clay samples, with added As^{+++} carrier, are dissolved with hydrofluoric and perchloric acids and hydrogen peroxide, and the silicon tetrafluoride evaporated off. The residue was taken up in hydrochloric acid and arsenic was separated by a hydrogen bromide distillation; the procedure henceforth was the same as that used for liquid samples.

X-Ray Fluorescence Method for Mg, Al, Si, Ca, K, Ti, Fe, and P

(John Kuhn and Ray Henderson)

The column section samples and clays were air dried then ground to ~200 mesh and oven dried at 105° C for 6 hours. From the dried sample, 125 mg was weighed into a graphite crucible containing 1.000 g of lithium tetraborate. A depression made in the tetraborate prior to addition of the sample prevented its contact with the crucible wall. Next, 125 mg of lanthanum oxide was added as a heavy-element absorber, and the contents of the crucible were mixed, with a glass rod, as thoroughly as possible without scraping the crucible wall or bottom. The mixture was fused in a furnace for 15 minutes at 1000° C, removed, covered with a second crucible and allowed to cool to room temperature. The resulting fused pellet was weighed alone to determine fusion loss and placed in the grinding vial of a No. 6 Wig-L-Bug with 2 percent by weight of Somar Mix (a commercial mixture used as a grinding and plasticizing agent). The sample was ground for 3 minutes, transferred to a die, and pressed at 40,000 psi. Samples were then exposed to X-rays and the data compared to values acquired from standard rock pellets prepared in the same manner. The resulting concentrations determined on the samples are quantitative for those major and minor elements listed (Mg, Al, Si, Ca, K, Ti, Fe, and P).

Optical Emission Spectrometry Method for Be, V, Cr, Co, Ni, Cu, and Mo

(Gary Dreher)

Direct reading optical emission spectrometry was used to determine trace element concentrations in the original clay materials. The procedure used was to prepare a mixture of 1 part $Ba(NO_3)_2$ (5 mg), 8 parts sample (40 mg) and 31 parts SPEX graphite powder (Spex Industries, Inc.) (155 mg) in a 1/2 inch diameter, 1 inch long polystyrene vial containing two 1/8 inch diameter polystyrene beads. The sample mixture was shaken in a Wig-L-Bug for 60 seconds. Fifteen milligrams of this mixture was loaded into each of 4 electrodes, 1/8 inch in diameter, having thin wall craters. The sample electrodes were arced at 15 A. short-circuit current for 65 seconds with an arc gap of 4 mm, and surrounded by a 10 SCFH flow of a gas mixture 80% in argon and 20% in oxygen.

Determination of Total Carbon (TC), Inorganic Carbon (IC), and Organic

Carbon (OC)

(David Heck and Larry Kohlenberger)

Total Carbon (TC) and Inorganic Carbon (IC) were determined in the column sections and clay samples. Organic Carbon (OC) was determined by difference of TC and IC. The procedures are as follows:

Total Carbon

A zirconium silicate combustion boat containing a layer of dry alumina powder (to prevent sample fusion to boat) is accurately weighed. A layer of sample (1.5 to .30 g) is added, and the boat is reweighed in order to obtain the sample weight. A Nesbitt absorption bulb containing a bottom layer of magnesium perchlorate and topped with CO_2 absorbent (lithasorb or ascarite) is also weighed. The weighed absorption bulb is placed on the exit end of a zirconium silicate combustion tube which is heated to 1350° C in a high temperature furnace. With dry oxygen flowing through the tube continuously, the sample boat is slowly pushed into the hot zone at a rate which will neither crack the boat nor blow out the sample. After the sample has been in the hot zone for 4 minutes, the sample boat is removed, the absorption bulb closed off, and the sample allowed to cool. It is reweighed, the CO_2 absorbed determined by difference, and % total carbon calculated.

Inorganic Carbon

A modified ASTM (1968) procedure, D 1756, is used whereby CO_2 is formed by decomposing ~0.5 g sample with acid and absorbing the gas on Lithosorb.

Methods for NH_4^+, TDS, COD, and Chloride

(Don Dickerson)

Ammonium ion (NH_4^+) was determined in the filtered (but not acidified) leachate samples as follows. A suitable volume of leachate (1 ml 0.01 N HCl is equivalent to 180 mg NH_4^+/liter) is placed in a Kjeldahl flask and diluted to ~20 ml with NH_4^+ free water. The flask is connected to the Kjeldahl distillation apparatus. The receiver contains 30 ml of 4% boric acid solution. Fifty percent KOH solution is slowly added into the flask port followed by 5 ml of $NaOH-Na_2S_2O_3$ solution (25 g NaOH, 5 g $Na_2S_2O_3$, and 75 ml H_2O). The solution is steam distilled for 4 minutes after NH_4^+ starts coming over. Three drops of methyl red-bromocresol green indicator is added and the solution is immediately titrated to the orange-pink end point with 0.01 N HCl solution.

Determination of Exchangeable NH_4^+

Exchangeable NH_4^+ was determined on the column sections according to a modified procedure by Jackson (1958). One sample (containing approximately .8 - 1.0 mg NH_4^+) is analyzed by the normal Kjeldahl procedure. A second sample is combined with 20 ml of 1.0 N, acidified NaCl and distilled similarily following the Kjeldohl procedure.

Determination of Chloride

Chloride was determined in the filtered (but not acidified) leachate samples as follows. A sample containing not more than 4 mg of Cl^- is diluted to 25 ml with Cl-free water and then combined with 25 ml of isopropyl alcohol. While stirring, 2 drops of bromophenol blue is added and the pH adjusted to slightly acid by the addition of 1.0 N NaOH solutions or 1.0 N HNO_3 solutions as needed. One half ml of a saturated solution of diphenyl carbazone in isopropyl alcohol is added and the solution titrated to the endpoint with 0.1 N Hg^{++} (as $Hg(NO_3)_2$ in dilute HNO_3).

Determination of Chemical Oxygen Demand (COD)

The following procedure, adopted from Leithe, (1947) was used to analyze filtered (but not acidified) leachate samples. A 1-10 ml leachate sample diluted to 50 ml with distilled water and 25 ml 0.10 N $K_2Cr_2O_7$ solution was added to 0.5 g $HgSO_4$ in a 300-ml ground-joint flask with a Friedrich condenser. Concentrated sulfuric acid (75 ml) containing 1 g Ag_2SO_4 was added in small portions with thorough swirling as well as two boiling stones as anti-bumping aids, and refluxing was carried out for 2 hours. The mixture was cooled, washed into a 500-ml Conical flask, diluted to 350 ml with distilled water, treated with 3 drops ferroin indicator and titrated with 0.1 N $Fe(NH_4)_2(SO_4)_2$ solution to a stable color change from blue-green to reddish-brown. A blank value was determined using 50 ml of distilled water under the same conditions.

Determination of Total Dissolved Solids (TDS)

TDS was determined in the filtered (but not acidified) leachate samples as follows. Ten ml was placed in a weighed beaker, covered with a watch-glass, and placed in an oven preheated to 250° F until evaporation was completed. The temperature was then raised to 350-375° C for an hour. The residue was finally cooled in a vacuum desicator and weighed.

Methods for Sulfate, Phosphate, and Boron

(David Heck)

Sulfate was determined in the original leachate solutions as follows. Fifty ml of sample was neutralized with concentrated HCl and then 0.5 ml added in excess and the sulfate precipitated in almost boiling solution with 10 ml of 10% $BaCl_2$ added drop by drop with constant stirring. After digesting one hour until the $BaSO_4$ settled, another drop of barium chloride was added to make sure the precipitation was complete, and the $BaSO_4$ filtered off, washed with hot water, ignited in the muffle furnace one hour at 1000° C and weighed as $BaSO_4$.

Determination of Phosphate

Phosphate ion was determined in the original leachate solutions as follows. Fifty ml of sample was brought to boil with 15 cc HNO_3 and 40 cc H_2O, digested for an hour, cooled, filtered. The filtered material was washed with a dilute HNO_3-NH_4NO_3 solution. The residue was discarded, the filtrates were combined and 11 ml ammonium citrimolybdate reagent added, brought cautiously to a boil, and then let to stand overnight. The resulting precipitate was filtered through a fritted crucible, washed with the above solution and water, dried at 100-105° C, cooled, and weighed.

Determination of Boron

Boron was determined on the column sections and clay samples according to the following procedure.

A 25-50 mg solid sample was weighted into a clean 4 oz. plastic bottle, and 10 ml of 2.5 NH_2SO_4 and 4 ml 5% HF added. The bottle was fitted with a tight cap, swirled, and allowed to stand overnight. The sample was diluted to a total volume of 20 ml, and 10 ml of .001 M methylene Blue (.374 g/l) and 25 ml of purified ethylene dichloride added. The bottle was shaken for at least 30 minutes, removed from shaker, and layers allowed to separate. A 5 ml portion of the lower layer was pipetted into a 25 ml volumetric flask and diluted to volume with ethylene dichloride. Unknown sample was then compared to known standards (1-6 ppm range) on a Beckman DBG Spectrophotometer at 660 µm. A reagent blank was required for standards and samples. Boron was determined in the leachate fractions according to the same procedure, however, two ml were used as the sample.

Determination of Base Exchange Capacity

(Bill Armon)

Base Exchange Capacity was determined on the column sections according to a procedure by Peech (1947), with slight modification. The 10 g sample was leached with ammonium acetate to remove exchangeable cations and to saturate the exchange complex with ammonia. The excess ammonia was removed by leaching with ethyl alcohol and the remaining, exchangeable ammonia removed and determined by distillation in a Kjeldahl apparatus.

Determination of Surface Area

(Joe Thomas)

The surface areas of the clays were determined by the B.E.T. method (Brunauer, Emmett, and Teller, 1938) using nitrogen as the adsorbate in a continuous flow system (Nelsen and Eggertsen, 1958).